U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB80-150592

Source Assessment Manufacture of Acetone and Phenol from Cumene

Monsanto Research Corp, Dayton, OH

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

May 79

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-79-019d
May 1979

PB80-150592

Research and Development

EPA

Source Assessment:
Manufacture of Acetone and Phenol from Cumene

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/2-79-019d

2.

3. RECI

PB 80 150592

4. TITLE AND SUBTITLE
SOURCE ASSESSMENT: Manufacture of Acetone and Phenol from Cumene

5. REPORT DATE
May 1979

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J.L. Delaney and T.W. Hughes

8. PERFORMING ORGANIZATION REPORT NO.
MRC-DA-889

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Monsanto Research Corporation
1515 Nicholas Road
Dayton, Ohio 45407

10. PROGRAM ELEMENT NO.
1AB015; ROAP 21AXM-071

11. CONTRACT/GRANT NO.
68-02-1874

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Task Final; 2/76 - 4/78

14. SPONSORING AGENCY CODE
EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Bruce A. Tichenor, MD-62, 919/541-2547. Other source assessment reports are in this series and in EPA-600/2-76-032, -77-107, and -78-004 series.

16. ABSTRACT The report describes a study of atmospheric emissions resulting from the manufacture of acetone and phenol from cumene. The air emissions from such manufacture consist only of hydrocarbons (HC). Emission factors are given for each species emitted to the atmosphere from each source within a typical plant. Emissions data are used to calculate several factors designed to quantify the hazard potential of the emissions. Industry contributions to atmospheric HC emissions from stationary sources are estimated to be: 0.023% for the Nation, 0.0049% for California, 0.013% for Illinois, 0.050% for Kansas, 0.084% for Louisiana, 0.034% for New Jersey, 0.049% for Ohio, 0.084% for Pennsylvania, and 0.081% for Texas. A variety of HC emission control methods are used, depending on the emission and the emission point. The two process technologies in use in the U.S. for oxidizing cumene to cumene hydroperoxide and for cleavage of the cumene hydroperoxide to acetone and phenol are discussed and compared. Process descriptions and flow sheets for these technologies are presented. Economic and production trends in the phenol industry and in the industries that use phenol, acetone, and the other byproducts are discussed and analyzed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Hydrocarbons	Pollution Control	13B
Assessments		Stationary Sources	14B
Industrial Processes			13H
Acetone			07C
Phenols			
Cumene			

18. DISTRIBUTION STATEMENT
Unlimited

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
200

22. PRICE
IMF

EPA Form 2220-1 (9-73)

EPA-600/2-79-019d
May 1979

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Contract No. 68-02-1874
Program Element No. 1AB015; ROAP 21AXM-071

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility to develop control technology for a large number of operations (more than 500) in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient environmental risk associated with the process to require emissions reduction. This report contains the data necessary to make that decision for the air emissions from the manufacture of acetone and phenol from cumene.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. In this study of the manufacture of acetone and phenol from cumene, Mr. Edward J. Wooldridge, Dr. I. Atly Jefcoat and Dr. Bruce Tichenor served as EPA Task Leaders.

ABSTRACT

This report describes a study of atmospheric emissions resulting from the manufacture of acetone and phenol from cumene.

The air emissions from such manufacture consist only of hydrocarbons. The potential environmental effect of these emissions is evaluated by estimating the source severity, defined as a ratio of the maximum time-averaged ground level concentration of a pollutant to an acceptable concentration. The source severities of total nonmethane hydrocarbons for a representative source having 136 x 10^3 metric tons of annual phenol capacity are: 3.5 for the cumene peroxidation vent, 0.58 for the combined cleavage section vents, 0.96 for the combined product purification section vents, 0.13 for the combined storage tank vents, 1.2 for the combined product transport loading vents, and 0.58 for fugitive sources.

Source severities greater than 0.05 for chemical substances are: 0.43 for benzene from the cumene peroxidation vent, 0.23 and 0.066 for cumene from the cumene peroxidation vent and the cleavage section vents combined, 0.13 for the heavy ends storage tank emission (assumed to be phenol), 0.17 for phenol from the phenol storage tanks, and 1.3 for phenol from the product loading vents combined.

Industry contributions to atmospheric hydrocarbon emissions from stationary sources are estimated to be: 0.023% for the nation, 0.0049% for California, 0.013% for Illinois, 0.050% for Kansas, 0.034% for Louisiana, 0.034% for New Jersey, 0.049% for Ohio, 0.084% for Pennsylvania, and 0.081% for Texas.

A variety of hydrocarbon emission control methods are used depending on the emission and emission point.

The two process technologies in use in the United States for oxidizing cumene to cumene hydroperoxide and for cleavage of the cumene hydroperoxide to acetone and phenol are discussed and compared. These technologies are those of Allied Chemical Corp. and Hercules, Inc. Economic and production trends in the phenol industry and in the industries that use phenol acetone, and the other byproducts are discussed and analyzed.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The study described in this report covers the period February 1976 to April 1978.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AA -- atomic absorption

GC -- gas chromatography

GC/FID -- gas chromatography with flame ionization detection

GC/MS -- gas chromatography/mass spectroscopy

FID -- flame ionization detector

HVOSS -- high volume organic sampling system

MS -- mass spectroscopy

SASS -- source assessment sampling system

SSMS -- spark source mass spectroscopy

TLV -- threshold limit value, mg/m^3

SYMBOLS

a -- variable in horizontal dispersion equation

A -- area, km^2

A_R -- $Q/ac\pi u$

B_R -- $-H^2/2c^2$

c -- variable in horizontal dispersion equation

C -- diameter factor

C_c -- gram moles of carbon that a gram mole of material contains

C_i -- phenol production capacity of plant i, metric tons/yr

C_t -- tank capacity, gal/tank

Cap -- representative source phenol capacity, kg/yr

CAP -- production capacity for the material, tons/yr

Caps -- total capacity on a state or national basis, metric tons/yr

d -- variable in vertical dispersion equation

D -- tank diameter, ft

ABBREVIATIONS AND SYMBOLS (continued)

D_i -- inside stack diameter, m

D_P -- population density, persons/km^2

$\bar{D}_P$ -- capacity weighted mean county population density, persons/km^2

D_{Pi} -- county population density for plant i, persons/km^2

e -- 2.72

E -- emission factor, g/kg phenol produced

E' -- emission factor, lb/ton phenol produced

E_s -- g of stack gas per kg phenol produced

EF_T -- total emission factor for nonmethane hydrocarbons, g/kg phenol produced

f -- degrees of freedom

f' -- variable in vertical dispersion equation

F -- hazard factor, g/m^3

F_g -- equivalent gasoline working loss, bbl/yr

F_p -- paint factor

G -- conversion factor, 1/300

h -- tank height, ft

h' -- physical stack height, m

H -- effective emission height, m

H' -- average tank outage, ft

ΔH -- plume size, m

k_1 -- conversion factor, yr/s

k_2 -- conversion factor, gal/ft

k_3 -- conversion factor, lb/ton

k_4 -- conversion factor, kg/g

k_5 -- conversion factor, m^3/g mole

K_p -- paint factor

K_s -- seal factor

K_t -- tank factor

K_T -- turnover factor

L -- total petrochemical loss, bbl

L_1 -- total petrochemical loss, lb/yr

ABBREVIATIONS AND SYMBOLS (continued)

L_g -- total equivalent gasoline loss, bbl/yr
L_y -- equivalent gasoline breathing loss, bbl/yr
M -- molecular weight, g/g mole, kg/kg mole, lb/lb mole
M_c -- material molecular weight, g/g mole, kg/kg mole, lb/lb mole
M_m -- molecular weight of methane, g/g mole, equivalent lb/lb mole
M_s -- molecular weight of stack gas, g/g mole
MEEF -- methane equivalent emission factor, g equivalent methane/kg phenol produced
n -- number items averaged
N -- number of turnovers per year
N' -- number of tanks
P -- vapor pressure of material stored at bulk temperature, psia
P -- atmosphere pressure, mb
P_s -- stack gas pressure, KPa
Q -- mass emission rate, g/s
R -- universal gas constant, $\frac{\text{KPa} \bullet \text{m}^3}{\text{g mole} \bullet {}^\circ\text{K}}$
s -- standard deviation
S -- source severity
t -- value from statistical tables for "Student t" distribution
T -- throughput per year of the stored material, gal/yr
T_a -- ambient temperature, °K
T_s -- stack gas temperature, °K
TE -- total emissions of hydrocarbons from stationary sources on a state or national, metric ton/yr
t_1, t_o -- averaging time, min
u -- wind speed, m/s
U -- utilization
$\bar{u}$ -- average wind speed, m/s
$\bar{u}$ -- average wind speed, mph
V -- tank capacity, bbl
V' -- volume liquid withdrawn from tank, bbl

SECTION 1

INTRODUCTION

The purpose of this document is to supply the data base necessary for the assessment of emissions from the manufacture of acetone and phenol from cumene. This document has been prepared from information compiled from literature, industry contact, field sampling and contact with Federal and state environmental protection agencies.

Phenol is an industrially important synthetic organic chemical intermediate whose main uses are in production of resins, caprolactam, and bisphenol A. Currently, the major industrial route to phenol is the peroxidation of cumene, although three other processes are also presently used in the United States (sulfonation of benzene, chlorination of benzene, and oxidation of toluene). Cumene peroxidation is now regarded as the only available process having future industrial significance.

In addition to phenol, acetone is produced as a coproduct. The main uses of acetone are in making methacrylate esters, protective coatings, methyl isobutyl ketone, and solvent derivatives. Acetone is produced by three other processes in the United States: 1) catalytic oxidation and dehydrogenation of isopropanol, 2) fermentation, and 3) propylene oxidation.

The cumene peroxidation process has two reaction steps: 1) oxidation of cumene with oxygen from air to cumene hydroperoxide, and 2) cleavage of cumene hydroperoxide by acid to phenol and acetone.

The major results of this study are summarized in Section 2 and include emission factors for materials emitted to the atmosphere from the emission points within a representative cumene peroxidation phenol plant. Also tabulated are several factors designed to measure the environmental hazard potential of the representative cumene peroxidation plant emissions and operations. These consist of source severity, industry contribution to total atmospheric emissions of criteria pollutants, the number of persons exposed to high contaminant levels, and future trends in emissions.

Section 3 provides a detailed description of the cumene peroxidation process, including process chemistry, major processing steps, flow diagrams, material balances, and geographic locations. The two process technologies using the cumene peroxidation reaction to produce acetone and phenol, the Allied process and the Hercules process, are discussed.

Atmospheric emissions from plants manufacturing acetone and phenol from cumene are discussed in Section 4. The species known to be emitted are detailed, and each emission point within the plant is described. Emission factors for each point and species are given. A representative source, a plant manufacturing acetone and phenol from cumene, is defined. The emission factors are used to determine source severity, calculate the industry contribution to total emissions of criteria pollutants, estimate the affected population, and determine future trends in emissions.

Section 5 considers the present and future aspects of pollution control technology. Emission controls presently installed at plants manufacturing acetone and phenol from cumene are discussed.

Economic and production trends in phenol and acetone manufacture, and in those industries that are major consumers of phenol and acetone, are analyzed in Section 6.

SECTION 2

SUMMARY

Phenol is currently manufactured in the United States by four processes: cumene peroxidation, benzene sulfonation, benzene chlorination, and toluene oxidation. Acetone is also currently manufactured in the United States by four processes: cumene peroxidation, isopropanol oxidation and dehydrogenation, fermentation, and propylene oxidation. The cumene peroxidation process is the major producer of phenol and acetone, a coproduct. Table 1 lists the production in 1975 and the capacities in 1977 for total acetone and phenol and for cumene-based acetone and phenol.[a,b]

TABLE 1. 1975 PRODUCTION AND 1977 CAPACITY FOR PHENOL AND ACETONE

Material	Production, 1975[a,b]		Capacity, 1977[b]	
	10^3 metric tons	Percent	10^3 metric tons	Percent
Phenol, total	792	100	1,470	100
Phenol, cumene based	703	89	1,360	93
Acetone, total	744	100	1,380	100
Acetone, cumene based	432	58	830	60

[a] Last year for which cumene-based production was reported separately.

[b] Puerto Rico is not included in this study. Capacity information for Puerto Rico has been excluded, but Puerto Rican production is not reported separately, and therefore cannot be excluded.

There are 10 plants manufacturing phenol from cumene in the continental United States. The plants are located in rural and nonrural counties having population densities of 10 to 5,836 persons/km^2.

Cumene is oxidized to cumene hydroperoxide by liquid phase contact with air. The cumene hydroperoxide may be washed, depending on the process, then concentrated to 80% by weight or higher cumene hydroperoxide. Cleavage to acetone, phenol, and other byproducts occurs by contact with an acid catalyst in the cleavage section. The product stream is washed to remove the acid catalyst. In the product purification section, acetone, phenol, acetophenone, α-methylstyrene, light ends, heavy ends, and wastes are separated and purified. The acetone, phenol, and any byproducts in demand are sold or used captively.

Sources of emissions within plants manufacturing acetone and phenol from cumene are:

- Cumene peroxidation vent.
- Cleavage section vents, combined.
- Product purification vents, combined.
- Storage tank vents, combined.
- Product transport loading vents, combined.
- Fugitive sources.

The only criteria pollutant emitted to the atmosphere is nonmethane hydrocarbons. (There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used in this report is a recommended guideline for meeting the primary ambient air quality standard for photochemical oxidants.)

Process technology to produce phenol and acetone from cumene via peroxidation is licensed in the United States by Allied Chemical Corp., and Hercules Inc. Emissions from both processes are similar.

Emissions from the cumene peroxidation step are caused by volatile hydrocarbons present in the spent air off-gas. This step contacts cumene and air to form cumene hydroperoxide. This emission source accounts for 51% of the mass of emissions from this process (based on total nonmethane hydrocarbons). All plants use some form of emission control on this off-gas, with an average 81% efficiency (based on total nonmethane hydrocarbons).

Emissions from the cleavage section are vented nonmethane hydrocarbons. The major step in this section is the cleavage of cumene hydroperoxide to acetone and phenol using an acid catalyst. Various auxiliary operations, such as washes and concentrations, are also performed. The Allied process vents only the cumene hydroperoxide concentration step. The Hercules process vents the cumene hydroperoxide wash, the cumene hydroperoxide concentration, the cumene hydroperoxide cleavage, and the product stream wash. Some plants use condensation or absorption to control emissions from some or all of these vents, and some vents are uncontrolled.

Emissions from the product purification section are vented hydrocarbons from the columns separating and purifying product streams and recycle streams. These vents have emission controls.

Storage tanks are used to hold feedstock and products. Emissions from this area were determined by engineering estimates. The control methods used are floating roofs, vent condensers, sealed roofs, and conservation vents.

Emissions from product transport loading occur from the displacement of vapors in the item being filled. Absorption and vapor recovery are used for control. Not all plants control emissions from this source.

Fugitive emissions occur from pump seals, compressor seals, pipeline valves and flanges, relief valves, and process drains.

Emission factors are summarized in Table 2 for manufacture of acetone and phenol from cumene. The emission factors were used to generate a number of other factors designed to quantify the potential hazard of production acetone and phenol from cumene.

To assess the impact of atmospheric emissions from the manufacture of acetone and phenol from cumene, the source severity for each material emitted from each emission point was estimated. Source severity is defined as the pollutant concentration to which the population may be exposed divided by an "acceptable concentration." The exposure concentration is the maximum time-averaged ground level concentration as determined by Gaussian plume dispersion methodology. The "acceptable concentration" is that pollutant concentration at which an incipient adverse health reaction is assumed to occur. The "acceptable concentration" is defined as the corresponding primary ambient air quality standard for criteria pollutants, and as a surrogate air quality standard for chemical substances determined by reducing threshold limit values (TLVs®) using an appropriate safety factor.

Source severities were calculated for a representative source, which is a plant producing acetone and phenol from cumene with a phenol capacity of 136 x 10^3 metric tons per year. The plant is utilized at 80% of production capacity. The capacities of the 10 plants producing phenol from cumene in the continental United States range from 25 x 10^3 metric tons/yr to 272 x 10^3 metric tons/yr of phenol. The source severities for the representative plant are presented in Table 3.

The maximum source severity was 3.5 for total nonmethane hydrocarbons, in methane equivalents, from the cumene peroxidation vent.

Atmospheric emissions of nonmethane hydrocarbons in methane equiv- from the manufacture of acetone and phenol from cumene in 1977 were estimated to be 3,900 metric tons. This is 0.024% of the total hydrocarbon emissions from stationary sources.

The percentages of total hydrocarbons from stationary sources attributable to nonmethane hydrocarbon emissions, in methane equivalents, from the manufacture of acetone and phenol from cumene were estimated for the individual states and the nation and are listed in Table 4.

TABLE 2. AVERAGE EMISSION FACTORS FOR THE MANUFACTURE OF ACETONE AND PHENOL FROM CUMENE BY EMISSION SOURCE, 1977

Material	Emission factors, g/kg of phenol produced					
	Cumene peroxidation vent[a]	Cleavage section vents, combined[a,b,c]	Product purification vents, combined[d,e]	Storage tank vents combined[f,g]	Product transport loading vents, combined[h,i]	Fugitive emissions[j]
Criteria pollutants:[k]						
Total nonmethane hydrocarbons[l]	1.8	0.17	1.2 ± 53%[m]	0.14	0.17	0.022
Chemical substances:						
Acetaldehyde	<0.0021 $^{+320\%}_{-100\%}$[m]		–[n]			
Acetone	0.60 $^{+860\%}_{-100\%}$[m]	6.0×10^{-6}	–[n]	0.060	0.074	
Acetophenone	<0.0086	4.4×10^{-6}		0.000055		
Benzene	0.20 ± 9.4%[m,o]	3.1×10^{-5}[o]				
2-Butanone	0.050 $^{+300\%}_{-100\%}$	1.8×10^{-5}				
2-Butenal	<0.0055 $^{+460\%}_{-100\%}$[m]	8.5×10^{-8}				
t-Butylbenzene	<0.0022	2.3×10^{-5}				
Cumene	0.86 $^{+170\%}_{-100\%}$[m]	0.14	–[n]	0.028		
Dimethylstyrene	0.00005					
Ethylbenzene	0.00042	5.0×10^{-7}				
Formaldehyde	0.0010 $^{+520\%}_{-100\%}$[m]	$<2.6 \times 10^{-7}$				
2-Hydroxy-2-phenyl propane	<0.0009	3.4×10^{-6}				
Isopentanal		8.5×10^{-7}				
α-Methylstyrene	<0.0001[p]		–[n]	0.0020		
Naphthalene	<0.0001					
Phenol			–[n]	0.051[q]	0.11[r]	
Propanal	<0.011 $^{+240\%}_{-100\%}$[m]					

Note.—Blanks indicate no emissions for the sampled points and no emissions reported for the other sources.

[a] Sampling performed.

[b] Emissions are from 1 to 4 vents.

[c] Data are from industry sources for 1976 and 1977.

[d] Emissions are from 5 to 7 vents.

[e] Data used are from industry sources for 1976.

[f] There were assumed to be 4 acetone, 1 acetophenone, 3 cumene, 1 heavy ends, 1 α-methylstyrene, and 4 phenol tanks.

[g] Emission factors are calculated.

[h] Loading of 2 to 5 product types.

[i] Data used are from industry sources for 1975 and 1978.

[j] Data used are from industry sources for 1975. The fugitive emission estimate includes those from pumps and sewers only. The other sources of fugitive emissions are not included in this estimate.

[k] Only hydrocarbons (organic materials) are emitted.

[l] Emission factors for total nonmethane hydrocarbons do not equal the sum of all emission factors for all organic materials except methane. The total nonmethane hydrocarbon emission factor is the sum of the methane equivalent emission factors based on carbon content for all nonmethane organic materials.

[m] The 95% confidence level error bounds are calculated using the "Student t" distribution to determine t, and

$$\pm\% = \left(\frac{s \cdot t}{\sqrt{n}}\right)\frac{1}{\bar{x}}\ 100$$

[n] Qualitatively identified.

[o] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

[p] Assumed to be the α form. The gas chromatographic /mass spectroscopic (GC/MS) analysis does not distinguish among the forms.

[q] The emission from the heavy ends storage tanks was assumed to be phenol. The phenol storage tanks emission factor is the average of a calculated value and an estimate supplied by H. Walker, Monsanto Chemical Intermediates Co, Alvin, Texas, 6 September 1978.

[r] The emission factor is an average of two estimates.

TABLE 3. SOURCE SEVERITIES OF ATMOSPHERIC EMISSIONS FROM A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1977

Material	Source severity					
	Cumene peroxidation vent[a]	Cleavage section vents, combined[a,b,c]	Product purification vents, combined[d,e]	Storage tank vents combined[f,g]	Product transport loading vents, combined[h,i]	Fugitive emissions[j]
Criteria pollutants:[k]						
Total nonmethane hydrocarbons[l]	3.5	0.58	0.96	0.10	1.2	0.58
Chemical substances:[m]						
Acetaldehyde	<0.0076		–[n]			
Acetone	0.0090	1.6×10^{-7}	–[n]		0.0039	
Benzene	0.43	1.2×10^{-5}[o]				
2-Butanone	0.0055	3.5×10^{-7}				
Cumene	0.23	0.066	–[n]			
Ethylbenzene	0.000063	1.3×10^{-7}				
Formaldehyde	0.022	$<1.0 \times 10^{-5}$				
α-Methylstyrene	$<1.4 \times 10^{-5}$[p]		–[n]			
Naphthalene	<0.00013					
Phenol				0.17[q]	1.3[r]	

Note.—Blanks indicate no emissions for sampled plants and no reported emissions for the other sources.

[a] Sampling performed.

[b] Emissions are from 1 to 4 vents.

[c] Data are from industry sources for 1976 and 1977.

[d] Emissions are from 5 to 7 vents.

[e] Data used are from industry sources for 1976.

[f] Values used are for the 4 phenol tanks.

[g] Emission factors are calculated.

[h] Loading of 2 to 5 product types.

[i] Data used are from industry sources for 1975 and 1978.

[j] Data used are from industry sources for 1975. The fugitive emission estimate includes those from pumps and sewers only. The other sources of fugitive emissions are not included in this estimate.

[k] Only hydrocarbons (organic materials) are emitted.

[l] Source severity for total nonmethane hydrocarbons will not equal the source severity for the total of the nonmethane hydrocarbons emitted. Source severities for the nonmethane organic materials are based on the toxicity of the chemicals. The source severity for total nonmethane hydrocarbons is based on the guideline for meeting the primary ambient air quality standard for photochemical oxidants.

[m] Only substances which have a TLV are listed.

[n] Qualitatively identified.

[o] The benzene emission factors used are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

[p] Assumed to be the α form.

[q] The emission factor used is the average of a calculated value and an estimate supplied by H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 6 September 1978.

[r] The emission factor is an average of two estimates.

TABLE 4. ESTIMATED INDUSTRY CONTRIBUTION TO ATMOSPHERIC EMISSIONS OF HYDROCARBONS, 1977

Location	Percentage
United States	0.023
California	0.0049
Illinois	0.013
Kansas	0.050
Louisiana	0.034
New Jersey	0.034
Ohio	0.049
Pennsylvania	0.084
Texas	0.081

The affected population is determined for source severities greater than or equal to 0.1. The affected area is determined and then multiplied by the capacity weighted mean county population density. The county population is not uniformly distributed throughout the county; therefore, in the plant vicinity, the population density may be higher or lower than the average. The number of persons that may be exposed to concentration above 0.1 of the primary ambient air quality standard (i.e., recommended guideline) for hydrocarbons for emissions from the representative source manufacturing acetone and phenol from cumene is estimated to be 12,600.

In 1975, 703×10^3 metric tons of phenol was produced from cumene. The 1980 projected production of phenol from cumene is $1,100 \times 10^3$ metric tons. Thus, assuming the same level of control 1980 exists in 1980 as existed in 1975, emissions from the manufacture of acetone and phenol from cumene will increase by 56% over that period; i.e.,

$$\frac{\text{Emissions in 1980}}{\text{Emissions in 1975}} = \frac{1,100 \times 10^3}{703 \times 10^3} = 1.56$$

SECTION 3

SOURCE DESCRIPTION

In 1977, phenol and acetone were ranked 37th and 40th, respectively, by production volume of the major chemicals in the United States (1). Phenol is used in the production of phenolic resins, caprolactam, bisphenol A, adipic acid, and other chemicals (2). Acetone is used in the production of methacrylate esters, methyl isobutyl ketone, protective coatings, solvent derivatives, bisphenol A, and other chemicals (3). Four major processes are used in the United States to produce synthetic phenol. They are: 1) benzene chlorination, 2) benzene sulfonation, 3) toluene oxidation, and 4) cumene peroxidation (4). Synthetic acetone is also produced by four major processes in the United States: 1) isopropanol oxidation, 2) propylene oxidation, 3) fermentation, and 4) cumene peroxidation (5). The cumene peroxidation process has accounted for 93% of the installed continental U.S. synthetic phenol production capacity and 60% of the installed continental U.S. synthetic acetone production capacity (excluding Puerto Rico).

The process description in this section presents the cumene peroxidation process chemistry and technology. An average plant material balance is presented, and the geographical distribution is discussed.

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(1) Facts and Figures for the Chemical Industry. Chemical and Engineering News, 56(18):31-37, 1978.

(2) Chemical Profile, Phenol. Chemical Marketing Reporter, 213(6):9, 1978.

(3) Chemical Profile, Acetone. Chemical Marketing Reporter, 212(21):9, 1977.

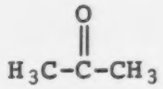
(4) Lowenheim, F. A., and M. K. Moran. Faith, Keyes, and Clarks Industrial Chemicals, Fourth Edition. John Wiley & Sons, Inc., New York, New York, 1975. 904 pp.

(5) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 1. John Wiley & Sons, Inc., New York, New York, 1963. 990 pp.

PROCESS DESCRIPTION

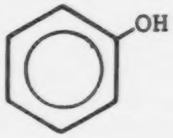
Major Chemical Descriptions

Acetone is a colorless, volatile, flammable liquid (5, 6). The structure of acetone is (6):

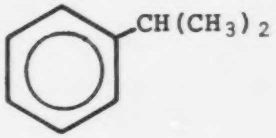


$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3$$

Phenol is a white crystalline solid which turns pink or red when contaminated (7). The solid can absorb moisture from the atmosphere and liquefy (7, 8). Phenol is toxic and has a distinctive odor (8). The structure of phenol is (6):



Cumene, the feed material, is a colorless, volatile, aromatic liquid (9).



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(6) Handbook of Chemistry and Physics, 52nd Edition, R. C. Weast, ed. Chemical Rubber Co., Cleveland, Ohio, 1971.

(7) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 15. John Wiley & Sons, Inc., New York, New York, 1968. 923 pp.

(8) Fleming, J. B., J. R. Lambrix, and J. R. Nixon. Safety in the Phenol from Cumene Process. Hydrocarbon Processing, 55(1):185-196, 1976.

(9) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 6. John Wiley & Sons, Inc., New York, New York, 1965. 932 pp.

Table 5 lists selected properties of cumene, acetone, phenol, and the important byproducts, α-methylstyrene and acetophenone (5-11).

TABLE 5. PROPERTIES OF MAJOR PRODUCTS, BYPRODUCTS AND FEED OF THE CUMENE PEROXIDATION PROCESS (5-11)

Material	Molecular weight	Freezing point, °C (@ 101.33 kPa)	Boiling point, °C (@ 101.33 kPa)	Density,[a] g/cm^3	Description	Vapor pressure, mm Hg
Phenol	94.1	40.9	181.75	1.0576	Toxic, colorless solid.	5.14 (@ 60°C)
Acetone	58.1	-95.35	52.6	0.[illegible]399	Volatile, colorless liquid.	200.04 (@ 25°C)
Cumene	120.2	-96	152.4	0.8618	Colorless liquid.	4.51 (@ 25°C)
α-Methylstyrene	118.2	24.5	163.4	0.9082	Colorless liquid.	3.92 (@ 30°C)
Acetophenone	120.2	20.5	202.0	1.0281	Monoclinic prisms or plates, usually liquid.	0.68 (@ 30°C)

[a] Density at 20°C referred to water at 4°C.

Process Chemistry

The main reaction is a two-step process (12). The first step is the liquid phase peroxidation of cumene hydroperoxide using oxygen from air (7, 12, 13). The second step is the cleavage of the cumene hydroperoxide to phenol and acetone (7, 12, 13). Figure 1 shows the stoichiometric reactions and the heats of reaction (7, 12, 14).

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(10) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 12. John Wiley & Sons, Inc., New York, New York, 1967. 905 pp.

(11) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 19. John Wiley & Sons, Inc., New York, New York, 1969. 839 pp.

(12) Pujado, P. R., J. R. Salazar, and C. V. Berger. Cheapest Route to Phenol. Hydrocarbon Processing, 55(3):91-96, 1976.

(13) Pervier, J. W., R. C. Barley, D. E. Field, B. M. Friedman, R. B. Morris, and W. A. Schwartz. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume III. EPA-450/3-73/005c (PB 245 629), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1974. 252 pp.

(14) Kiesling, W., I. Kraft, K. Moll, and K. Pelzing. Über die Reiningung von Phenol aus dem Cumolverfahren. Chemische Technik (Leipzig), 23(7):423-427, 1971.

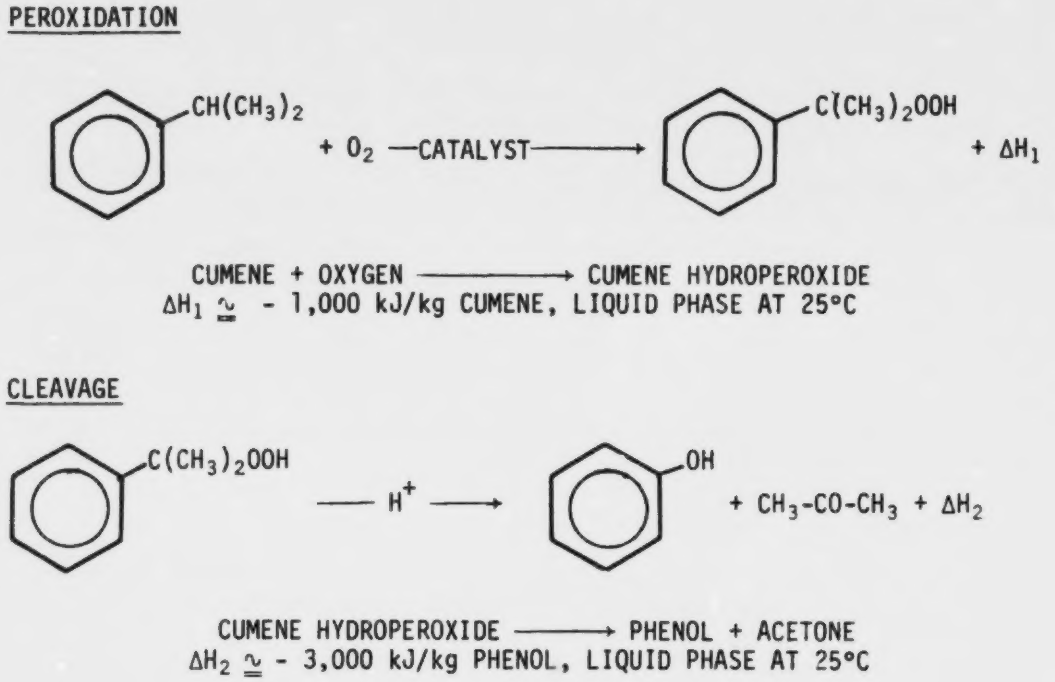
PEROXIDATION
CH(CH3)2
+ O2 —CATALYST→
C(CH3)2OOH
+ ΔH1
CUMENE + OXYGEN → CUMENE HYDROPEROXIDE
ΔH1 ≅ - 1,000 kJ/kg CUMENE, LIQUID PHASE AT 25°C
CLEAVAGE
C(CH3)2OOH
— H+ →
OH
+ CH3-CO-CH3 + ΔH2
CUMENE HYDROPEROXIDE → PHENOL + ACETONE
ΔH2 ≅ - 3,000 kJ/kg PHENOL, LIQUID PHASE AT 25°C

Figure 1. Chemistry of the main reactions in the cumene peroxidation process.

Side reactions, which produce acetophenone and α-methylstyrene, are shown in Figure 2 (7, 12, 14). The free radical form of oxygen, $O^{\cdot}$, is used because the oxygen produced by formation of 2-hydroxy-2-phenylpropane will be consumed in other reactions (personal communication with H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 7 October 1977). In addition, cumene impurities, such as alkylbenzene, can oxidize and cleave to form phenol and an aldehyde or ketone (e.g., acetaldehyde or ethyl methyl ketone) (14). Some of the α-methylstyrene and phenol are polymerized by the sulfuric acid catalyst. The hydrocarbons present will not sulfate under operating conditions. A small amount of α-methylstyrene may form styrene during the cleavage reaction. Styrene formation is not favored thermodynamically (personal communication with R. Canfield, Monsanto Chemical Intermediates Co., Alvin, Texas, 17 October 1977). The acidic conditions prevent the formation of styrene oxide, a known carcinogen (personal communication with G. A. Richardson, Monsanto Research Corporation, Dayton, Ohio, 4 August 1976).

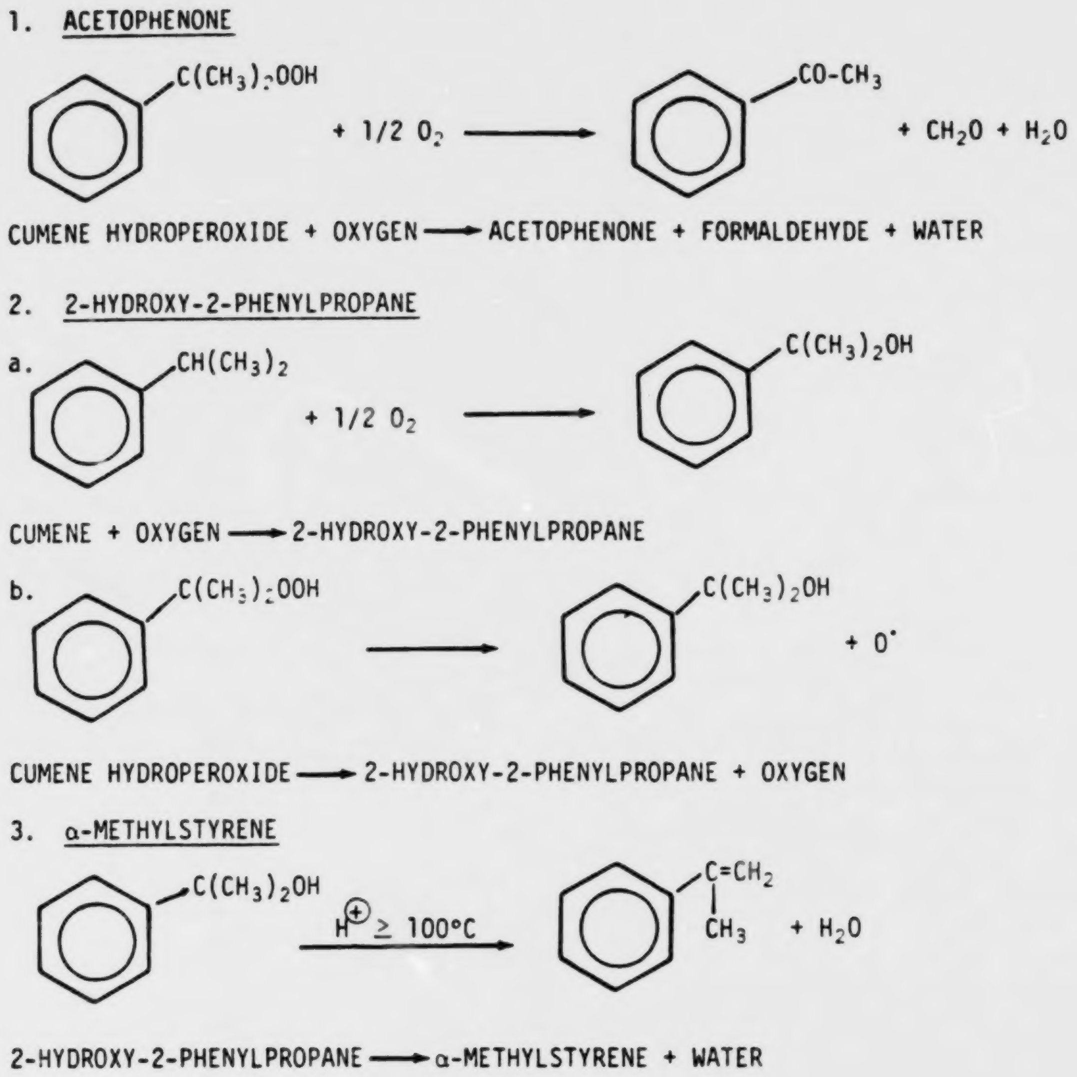
1. ACETOPHENONE
C(CH3)2OOH
+ 1/2 O2
CO-CH3
+ CH2O + H2O
CUMENE HYDROPEROXIDE + OXYGEN → ACETOPHENONE + FORMALDEHYDE + WATER
2. 2-HYDROXY-2-PHENYLPROPANE
a.
CH(CH3)2
+ 1/2 O2
C(CH3)2OH
CUMENE + OXYGEN → 2-HYDROXY-2-PHENYLPROPANE
b.
C(CH3)2OOH
C(CH3)2OH
+ O˙
CUMENE HYDROPEROXIDE → 2-HYDROXY-2-PHENYLPROPANE + OXYGEN
3. α-METHYLSTYRENE
C(CH3)2OH
H⊕ ≥ 100°C
C=CH2
CH3
+ H2O
2-HYDROXY-2-PHENYLPROPANE → α-METHYLSTYRENE + WATER

Figure 2. Main side reactions of the cumene peroxidation process.

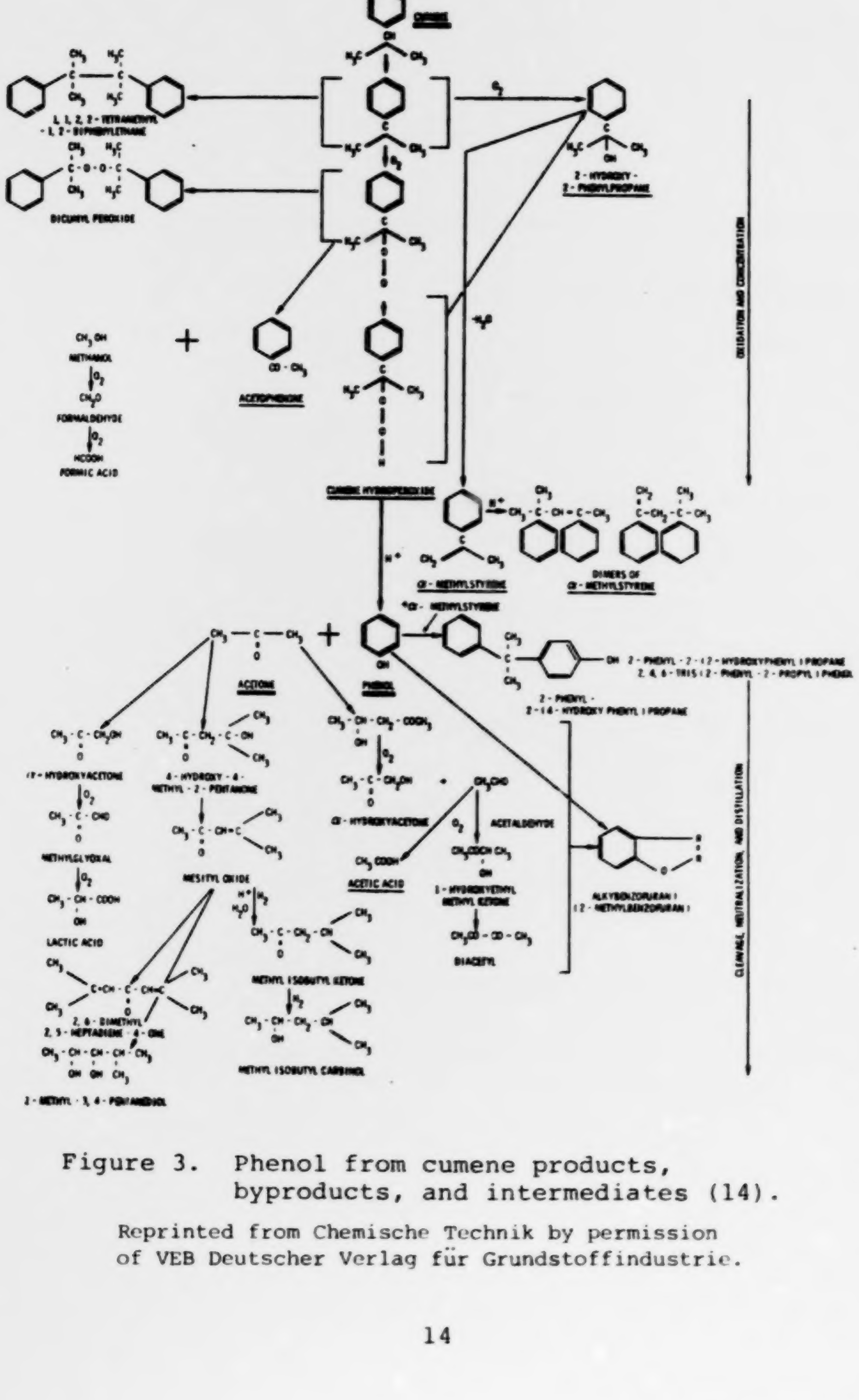
CUMENE
1,1,2,2-TETRAMETHYL-1,2-DIPHENYLETHANE
DICUMYL PEROXIDE
2-HYDROXY-2-PHENYLPROPANE
OXIDATION AND CONCENTRATION
METHANOL
FORMALDEHYDE
FORMIC ACID
ACETOPHENONE
CUMENE HYDROPEROXIDE
α-METHYLSTYRENE
DIMERS OF α-METHYLSTYRENE
ACETONE
PHENOL
METHYLGLYOXAL
LACTIC ACID
MESITYL OXIDE
METHYL ISOBUTYL KETONE
METHYL ISOBUTYL CARBINOL
ACETIC ACID
ACETALDEHYDE
DIACETYL
CLEAVAGE, NEUTRALIZATION, AND DISTILLATION

Figure 3. Phenol from cumene products, byproducts, and intermediates (14).

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The peroxidation reaction proceeds by a free radical mechanism with the selectivity for cumene hydroperoxide being greater at lower temperatures than at high temperatures (7, 8, 12). However, the reaction is faster at higher temperatures. The peroxidation reaction is autocatalytic, poisoned by phenols, and inhibited by unsaturated compounds, sulfur compounds, and styrene (7, 8, 12).

The cleavage reaction is instantaneous and 99.9% complete in the presence of sulfuric acid (8). Cumene hydroperoxide is stable at normal conditions, but decomposes rapidly upon exposure to copper, zinc, cobalt, acidic conditions, and/or high temperatures (greater than 140°C) (7, 8, 10). The decomposition reaction is autocatalytic (8).

Process Technology

There are two versions of the cumene peroxidation process presently licensed and in use in the United States. They were developed by Allied Chemical Corp. and Hercules, Inc. (15-19). The Allied technology represents 45% of the 1977 installed capacity for synthetic phenol production from cumene, and the Hercules technology represents 55% (excluding Puerto Rico).

Process flow diagrams of the Allied process and the Hercules process are shown in Figures 4 and 5 (8, 12, 15, 18-20 and personal communications with L. B. Evans, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 9 February 1976, and with H. Walker, 7 October 1977). Both processes exhibit the same general operation in the following areas:

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(15) Petrochemicals Handbook. Hydrocarbon Processing, 56(11): 193, 1977.

(16) Sittig, M. Organic Chemical Process Encyclopedia, Second Edition. Noyes Development Corporation, Park Ridge, New Jersey, 1969. 712 pp.

(17) Preparation of Aralkyl Hydroperoxides. Netherlands Application 64/08468 (to Allied Chemical Corporation), January 26, 1965.

(18) Cumene Oxidation. U.S. Pat. App. 214,864, August 6, 1962; British Patent 999,441 (to Allied Chemical Corporation), July 28, 1965.

(19) Feder, R. L., R. Fuhrmann, J. Pisanchyn, S. Elishewitz, T. H. Insinger, and C. T. Mathew. Continuous Process for Preparing Cumene Hydroperoxide. U.S. Patent 3,906,901 (to Allied Chemical Corporation), September 23, 1975.

(20) Stobaugh, R. B. Phenol: How, Where, Who - Future. Hydrocarbon Processing, 45(1):143-152, 1966.

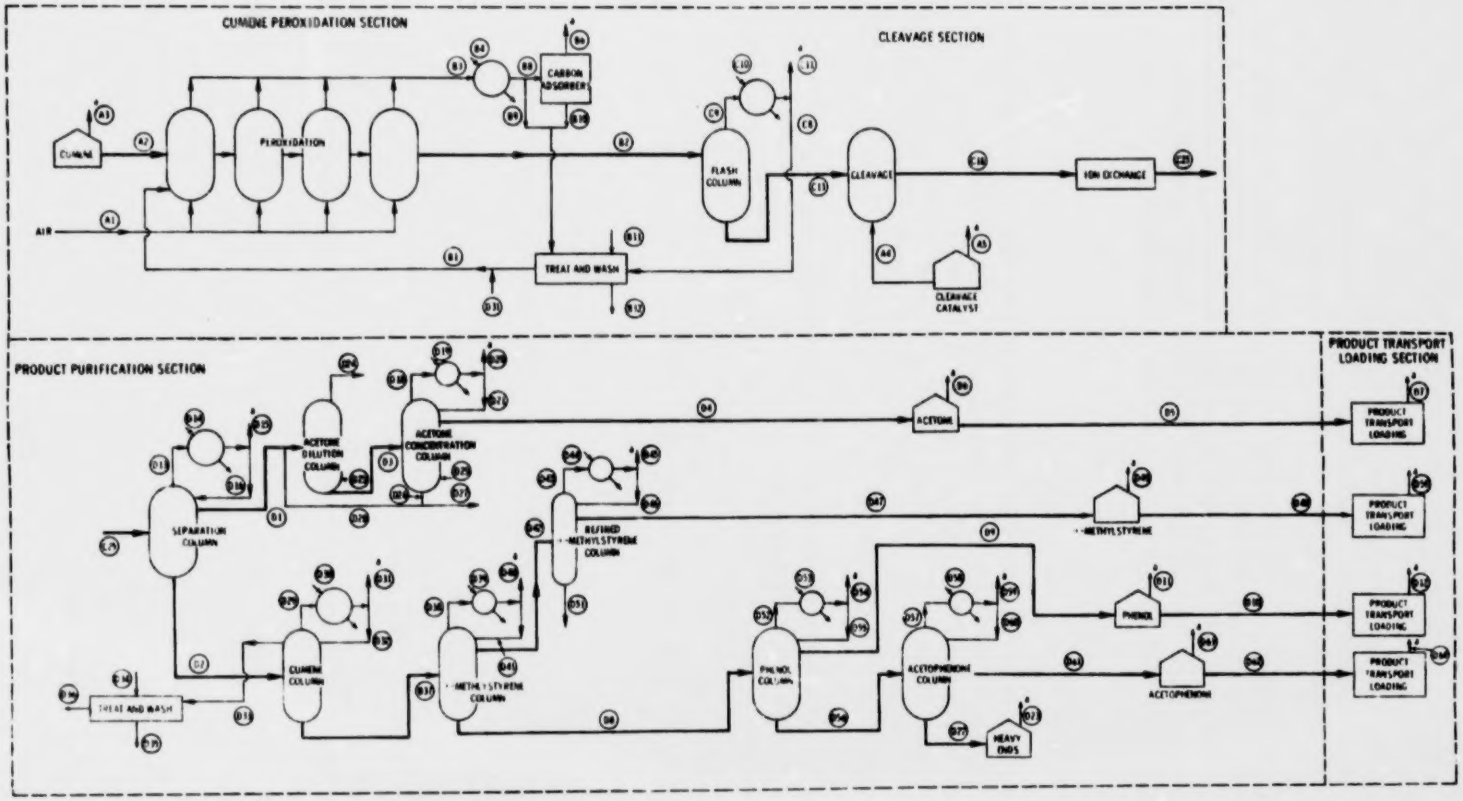
CUMENE PEROXIDATION SECTION
CLEAVAGE SECTION
CUMENE
AIR
PEROXIDATION
CARBON ADSORBER
TREAT AND WASH
FLASH COLUMN
CLEAVAGE
ION EXCHANGE
CLEAVAGE CATALYST
PRODUCT PURIFICATION SECTION
PRODUCT TRANSPORT LOADING SECTION
SEPARATION COLUMN
ACETONE DILUTION COLUMN
ACETONE CONCENTRATION COLUMN
ACETONE
REFINED METHYLSTYRENE COLUMN
METHYLSTYRENE
CUMENE COLUMN
METHYLSTYRENE COLUMN
PHENOL COLUMN
ACETOPHENONE COLUMN
PHENOL
ACETOPHENONE
HEAVY ENDS
TREAT AND WASH
PRODUCT TRANSPORT LOADING
PRODUCT TRANSPORT LOADING
PRODUCT TRANSPORT LOADING
PRODUCT TRANSPORT LOADING

Figure 4. Process flow diagram for the Allied Chemical process technology.

(continued)

Figure 4 (continued)

KEY

STREAM	IDENTIFICATION
A1	AIR
A2	FEED CUMENE
A3[a]	CUMENE STORAGE TANK EMISSIONS
A4	CLEAVAGE CATALYST
A5[a]	CLEAVAGE CATALYST STORAGE TANK EMISSION
B1	RECYCLE CUMENE, TREATED AND WASHED
B2	CUMENE AND CUMENE HYDROPEROXIDE
B3	SPENT GAS
B4	COOLING WATER
B6[a]	SPENT GAS AND HYDROCARBONS TO ATMOSPHERE
B7	RECYCLE CUMENE
B8	SPENT GAS AND NONCONDENSED VAPORS
B9	RECYCLE CUMENE
B10	RECYCLE CUMENE
B11	TREATING AND WASHING STREAM
B12	TREATING AND WASHING WASTES
C8	RECYCLE CUMENE
C9	VAPOR STREAM
C10	COOLING WATER
C11[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
C13	CONCENTRATED CUMENE HYDROPEROXIDE
C18	PRODUCT STREAM
C25	"WASHED" PRODUCT STREAM
D1	LIGHT FRACTION
D2	HEAVY FRACTION
D3	CRUDE ACETONE
D4	REFINED ACETONE
D5	ACETONE
D6[a]	ACETONE STORAGE TANK EMISSIONS
D7[a]	ACETONE TRANSPORT LOADING EMISSIONS
D8	CRUDE PHENOL
D9	REFINED PHENOL
D10	PHENOL
D11[a]	PHENOL STORAGE TANK EMISSIONS
D12[a]	PHENOL TRANSPORT LOADING EMISSIONS
D13	VAPORS
D14	COOLING WATER
D15[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D16	RECYCLED CONDENSATE
D18	VAPORS
D19	COOLING WATER
D20[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D21	RECYCLED CONDENSATE
D22	HEAVY ENDS
D23[a]	HEAVY ENDS STORAGE TANK EMISSIONS
D24	WASTES
D25	STEAM
D26	BOTTOMS
D27	WATER
D28	RECYCLE
D29	VAPORS
D30	COOLING WATER
D31[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D32	RECYCLED CONDENSATE
D33	RECYCLE CUMENE
D34	TREATING AND WASHING STREAM
D35	TREATING AND WASHING WASTES
D36	RECYCLE CUMENE, TREATED AND WASHED
D37	PRODUCT STREAM
D38	VAPORS
D39	COOLING WATER
D40[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D41	RECYCLED CONDENSATE
D42	CRUDE-α-METHYLSTYRENE
D43	VAPORS
D44	COOLING WATER
D45[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D46	RECYCLED CONDENSATE
D47	REFINED α-METHYLSTYRENE
D48	α-METHYLSTYRENE
D49[a]	α-METHYLSTYRENE STORAGE TANK EMISSIONS
D50[a]	α-METHYLSTYRENE TRANSPORT LOADING EMISSIONS
D51	RECYCLE
D52	VAPORS
D53	COOLING WATER
D54[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D55	RECYCLED CONDENSATE
D56	CRUDE ACETOPHENONE
D57	VAPORS
D58	COOLING WATER
D59[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D60	RECYCLED CONDENSATE
D61	REFINED ACETOPHENONE
D62	ACETOPHENONE
D63[a]	ACETOPHENONE STORAGE TANK EMISSIONS
D64[a]	ACETOPHENONE TRANSPORT LOADING EMISSIONS

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[a] EMISSION TO ATMOSPHERE.

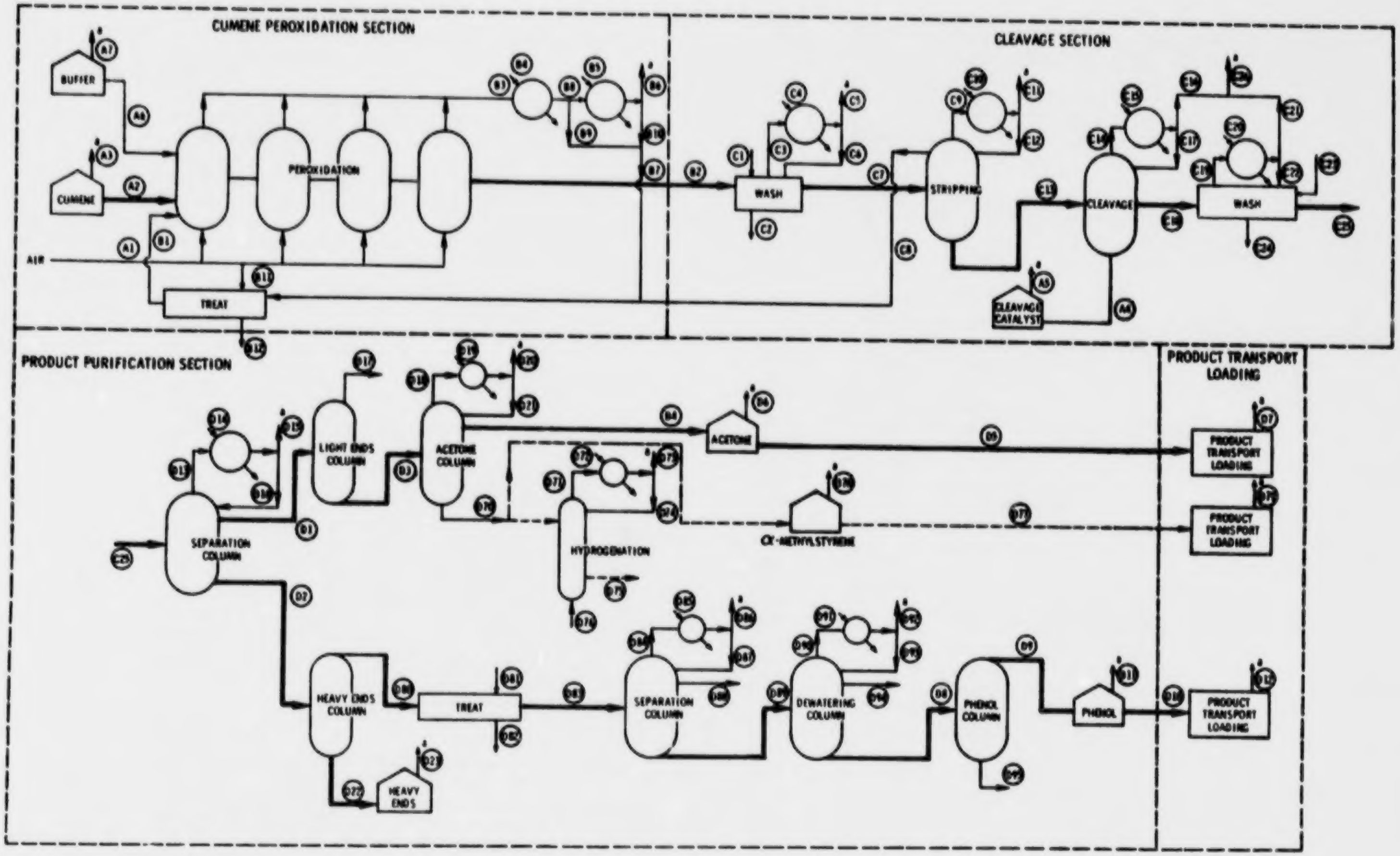

CUMENE PEROXIDATION SECTION
BUFFER
CUMENE
AIR
PEROXIDATION
TREAT
CLEAVAGE SECTION
WASH
STRIPPING
CLEAVAGE
CLEAVAGE CATALYST
WASH
PRODUCT PURIFICATION SECTION
SEPARATION COLUMN
LIGHT ENDS COLUMN
ACETONE COLUMN
ACETONE
HYDROGENATION
α-METHYLSTYRENE
HEAVY ENDS COLUMN
HEAVY ENDS
TREAT
SEPARATION COLUMN
DEWATERING COLUMN
PHENOL COLUMN
PHENOL
PRODUCT TRANSPORT LOADING
PRODUCT TRANSPORT LOADING
PRODUCT TRANSPORT LOADING
PRODUCT TRANSPORT LOADING

Figure 5. Process flow diagram for the Hercules process technology.

STREAM	IDENTIFICATION
A1	AIR
A2	FEED CUMENE
A3[a]	CUMENE STORAGE TANK EMISSIONS
A4	CLEAVAGE CATALYST
A5[a]	CLEAVAGE CATALYST STORAGE TANK EMISSION
A6	BUFFER
A7[a]	BUFFER STORAGE TANK EMISSION
B1	RECYCLE CUMENE, TREATED
B2	CUMENE AND CUMENE HYDROPEROXIDE
B3	SPENT GAS
B4	COOLING WATER
B5	REFRIGERANT
B6[a]	SPENT GAS AND HYDROCARBONS TO AIR
B7	RECYCLE CUMENE
B8	SPENT GAS AND NONCONDENSED VAPORS
B9	RECYCLE CUMENE
B10	RECYCLE CUMENE
B11	TREATING STREAM
B12	TREATING WASTES
C1	WASH WATER
C2	WASTEWATER
C3	VAPOR STREAM
C4	COOLING WATER
C5[a]	NONCONDENSABLE VAPOR TO ATMOSPHERE
C6	CONDENSATE RECYCLE
C7	WASHED CUMENE HYDROPEROXIDE
C8	RECYCLE CUMENE
C9	VAPOR STREAM
C10	COOLING WATER
C11[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
C12	CONDENSATE RECYCLE
C13	CONCENTRATED CUMENE HYDROPEROXIDE
C14	VAPOR STREAM
C15	COOLING WATER
C16	NONCONDENSABLE VAPORS
C17	CONDENSATE RECYCLE
C18	PRODUCT STREAM
C19	VAPOR STREAM
C20	COOLING WATER
C21	NONCONDENSABLE VAPORS
C22	CONDENSATE RECYCLE
C23	WASH WATER
C24	WASTEWATER
C25	WASHED PRODUCT STREAM
C26[a]	VAPORS TO ATMOSPHERE
D1	LIGHT FRACTION
D2	HEAVY FRACTION
D3	CRUDE ACETONE
D4	REFINED ACETONE
D5	ACETONE
D6[a]	ACETONE STORAGE TANK EMISSION
D7[a]	ACETONE TRANSPORT LOADING
D8	CRUDE PHENOL
D9	REFINED PHENOL
D10	PHENOL
D11[a]	PHENOL STORAGE TANK EMISSION
D12[a]	PHENOL PRODUCT LOADING
D13	VAPORS
D14	COOLING WATER
D15[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D16	RECYCLED CONDENSATE
D17	LIGHT ENDS
D18	VAPORS
D19	COOLING WATER
D20[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D21	RECYCLED CONDENSATE
D22	HEAVY ENDS
D23[a]	HEAVY ENDS STORAGE TANK EMISSION
D70	CRUDE α-METHYLSTYRENE
D71	VAPORS
D72	COOLING WATER
D73[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D74	RECYCLED CONDENSATE
D75	RECYCLE CUMENE
D76	HYDROGEN
D77	α-METHYLSTYRENE
D78[a]	α-METHYLSTYRENE STORAGE TANK EMISSION
D79[a]	α-METHYLSTYRENE TRANSPORT LOADING EMISSION
D80	MIDDLE FRACTION
D81	TREAT STREAM
D82	TREAT WASTES
D83	TREATED FRACTION
D84	VAPORS
D85	COOLING WATER
D86[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D87	RECYCLED CONDENSATE
D88	RECYCLE
D89	CRUDE WET PHENOL
D90	VAPORS
D91	COOLING WATER
D92[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D93	RECYCLED CONDENSATE
D94	WATER
D95	RECYCLE

---

[a] EMISSION TO ATMOSPHERE.

a) feed material preparation
b) cumene peroxidation
c) cleavage section
d) product purification
e) waste disposal
f) storage
g) product transport loading
h) intermittent emissions.

The flow diagrams are for the processing of cumene to phenol and acetone. Similar streams have similar stream numbers in the figures.

In the peroxidation section, the processes differ in that the Hercules process uses a buffer and the Allied process uses no promoters or additives. The Allied technology formerly involved the use of a suspended promoter and subsequent filtration (18, 19). The latest technology developed by Allied Chemical Corp., involves no promoter (19). The majority of the Allied licensees have converted to this technology or are planning the conversion (personal cummunication with L. A. Mattioli, Allied Chemical Corp., Marcus Hook, Pennsylvania, 14 October 1977). Therefore, the major design in use does not involve a filtration step to remove a suspended promoter.

In the cleavage section, the process differences between the two technologies are that the Allied process concentrates the cumene hydroperoxide by flash distillation, cleaves it to acetone and phenol with acid, and neutralizes the acid using ion exchange. The Hercules process washes the cumene hydroperoxide, concentrates it by stripping, cleaves the cumene hydroperoxide to acetone and phenol, and removes the acid by a water wash.

In the product purification section, the major process difference in the two process technologies is that the Allied process separates acetophenone but the Hercules process does not. There are also differences in the actual compositions of the exit streams from the columns in this section, but both designs separate acetone, phenol, α-methylstyrene (if desired), recycle streams, and heavy ends.

The following subsections describe the process operations in the Allied process and the Hercules process separately.

Allied Process Technology--

Feed materials preparation--The feed materials required are cumene, air, and cleavage catalyst. Feed material streams are designated with the letter A before the stream number.

The cumene (Stream A2 in Figures 4 and 5) must be at least 99.8% pure and may be obtained captively or on the open market (12, 14, 19, 20, and personal communication with L. B. Evans, 9 February

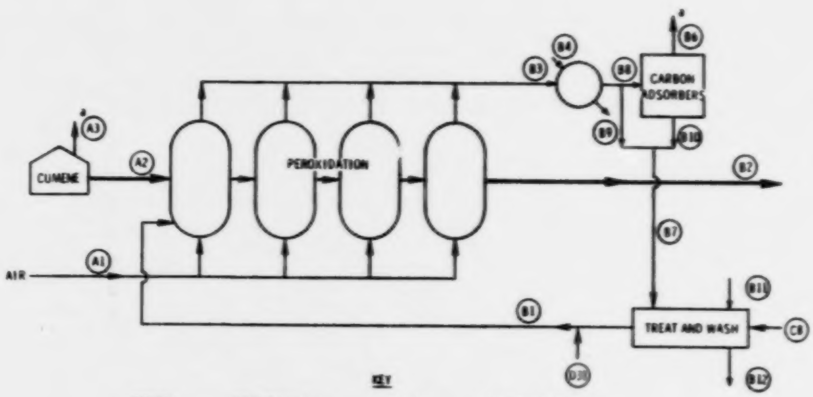
1976). If cumene is prepared captively, a purification step may be necessary. If so, that step is considered to be part of the manufacture of cumene, not phenol.

The air (Stream A1) is fed to the peroxidation vessels at slight pressure (18, 19). Air rather than oxygen is used because of economics (21).

The cleavage catalyst (Stream A4) is sulfuric acid. It is diluted before addition to the cleavage reactor with water, acetone, phenol, or another hydrocarbon or mixture of hydrocarbons (22).

Cumene peroxidation--Figure 6 shows this section of the Allied process technology. Streams in this section are designated with the letter B before the stream number.

CUMENE PEROXIDATION SECTION



KEY

STREAM	IDENTIFICATION	STREAM	IDENTIFICATION
A1	AIR	B6^a	SPENT GAS AND HYDROCARBONS TO ATMOSPHERE
A2	FEED CUMENE	B7	RECYCLE CUMENE
A3^a	CUMENE STORAGE TANK EMISSIONS	B8	SPENT GAS AND NONCONDENSED VAPORS
B1	RECYCLE CUMENE, TREATED AND WASHED	B9	RECYCLE CUMENE
B2	CUMENE AND CUMENE HYDROPEROXIDE	B10	RECYCLE CUMENE
B3	SPENT GAS	B11	TREATING AND WASHING STREAM
B4	COOLING WATER	B12	TREATING AND WASHING WASTES
		C8	RECYCLE CUMENE
		D31	RECYCLE CUMENE

^{a}EMISSION TO ATMOSPHERE

Figure 6. Cumene peroxidation section of the Allied Process.

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(21) Hedley, W. H., S. M. Mehta, C. M. Moscowitz, R. B. Reznik, G. A. Richardson, and D. L. Zanders. Potential Pollutants from Petrochemical Processes. Technomic Publishing Co., Westport, Connecticut, 1975. 362 pp.

(22) Gordon, J. What Are the Processes and Prospects for Phenol? Hydrocarbon Processing and Petroleum Refiner, 40(6):193-206, 1961.

In the cumene peroxidation area, feed cumene, recycle cumene, and air (Streams A2, B1, and A1) are fed to a vessel where cumene is peroxidized to cumene hydroperoxide in the liquid phase (7, 8, 14). The vessel is equipped for intimate gas-liquid contact, with the air stream providing agitation. The vessel cooling system is necessary to control the temperature by removing the approximately 1,400 kJ/kg of cumene heat of reaction (which includes the contribution of side reactions) (8, 12).

The air flow to the peroxidation step is at least 25% of the maximum oxygen requirement on a mole basis and where the exit gas contains 3% to 10% oxygen on a mole basis (19). That is, for each 1.00 kg of cumene, at least 0.32 kg of gas containing 21% oxygen is supplied.

Present economics favor the use of air rather than oxygen as the oxidizing gas. Future events could change that. The favorable aspects of oxygen use are the reduction in the total liquid entrainment and the smaller volumes of waste gas and vaporized hydrocarbons. Also, some equipment can be reduced in size. The favorable aspects of air use are the lower cost of air use as compared to buying oxygen, and safety considerations (13, 23). The explosive limits of cumene and air mixtures are shown in Figure 7 as a function of temperature and pressure (23).

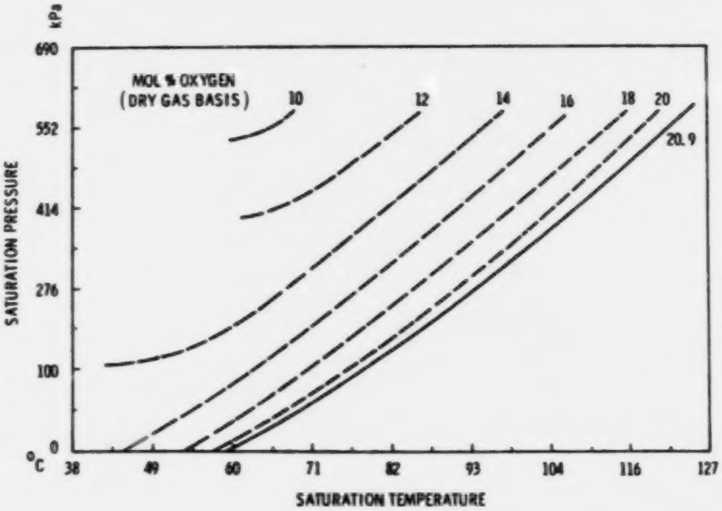

Figure 7. Upper explosive limits for the cumene-air system as a function of temperature and pressure (23).

Reprinted from Hydrocarbon Processing by permission of Gulf Publishing Co.

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(23) Saunby, J. B., and B. W. Kiff. Liquid-Phase Oxidation... Hydrocarbons to Petrochemical. Hydrocarbon Processing, 55(11):247-252, 1976.

The effects of kinetic and mass transfer rate limitations need to be investigated to determine whether air or oxygen is favored at operating conditions (23).

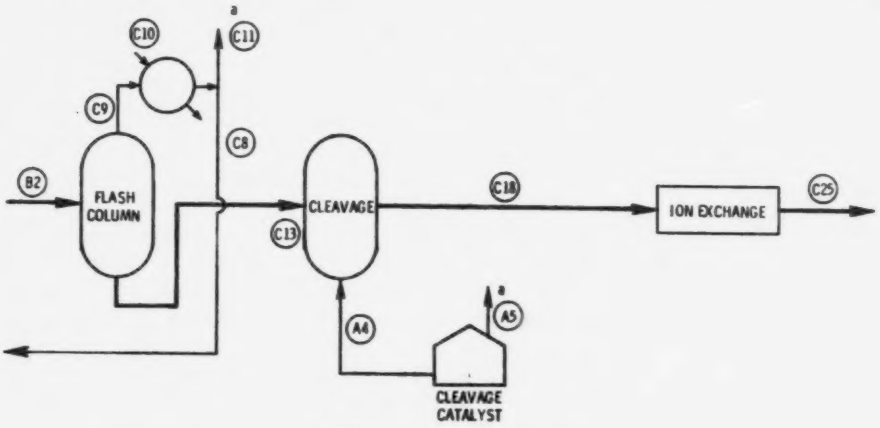
The operating temperatures decrease stepwise from 120°C to 80°C in the four reaction vessels (17-19).

Entrained cumene, vaporized cumene, and other vaporized organic materials are recovered from the waste gas exit stream (Stream B3) by condensation and carbon adsorption, and then recycled (Streams B7 and B1) after being treated and washed. The gas is released to the atmosphere (Stream B6).

Cleavage section--Figure 8 shows this section of the Allied Process technology. Streams in this section are designated by the letter C before the stream number.

The cumene hydroperoxide concentration area concentrates the relatively low concentration of cumene hydroperoxide in the stream (Stream B2) from the peroxidation section to 80% by weight or higher (7, 8, 12, 15, 19). Vacuum flash distillation separates the unreacted cumene (Stream B1) from the cumene hydroperoxide (Stream C13) for recycle after treating and washing. The noncondensable vapors (Stream C11) are vented to the atmosphere.

CLEAVAGE SECTION



KEY

STREAM	IDENTIFICATION	STREAM	IDENTIFICATION
A4	CLEAVAGE CATALYST	C10	COOLING WATER
A5[a]	CLEAVAGE CATALYST STORAGE TANK EMISSION	C11[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
B2	CUMENE AND CUMENE HYDROPEROXIDE	C13	CONCENTRATED CUMENE HYDROPEROXIDE
C8	RECYCLE CUMENE	C18	PRODUCT STREAM
C9	VAPOR STREAM	C25	"WASHED" PRODUCT STREAM

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[a] EMISSION TO ATMOSPHERE

Figure 8. Cleavage section of the Allied process.

In the cleavage area, the concentrated cumene hydroperoxide (Stream C13) is cleaved to acetone and phenol (Stream C18) in the presence of sulfuric acid (Stream A4) or other strong mineral acid (12).

Details of the cleavage reactors are not available in the technical literature. However, no streams are vented to the atmosphere (personal communication with L. B. Evans, 9 February 1976).

The acid cleavage catalyst is neutralized by ion exchange. There is no emission from this operation (personal communication with L. B. Evans, 9 February 1976).

Product purification--The product stream (Stream C25) at this point contains phenol, acetone, cumene, acetophenone, α-methylstyrene, and other materials. The recovery and purification section consists of numerous columns. Streams in this section are designated by the letter D before the stream number.

Figure 9 shows this section of the Allied process technology.

The products (Stream C25) are fed to a separation column which produces a light fraction (Stream D1) and a heavy fraction (Stream D2). The noncondensable vapors are vented to the atmosphere (Stream D15).

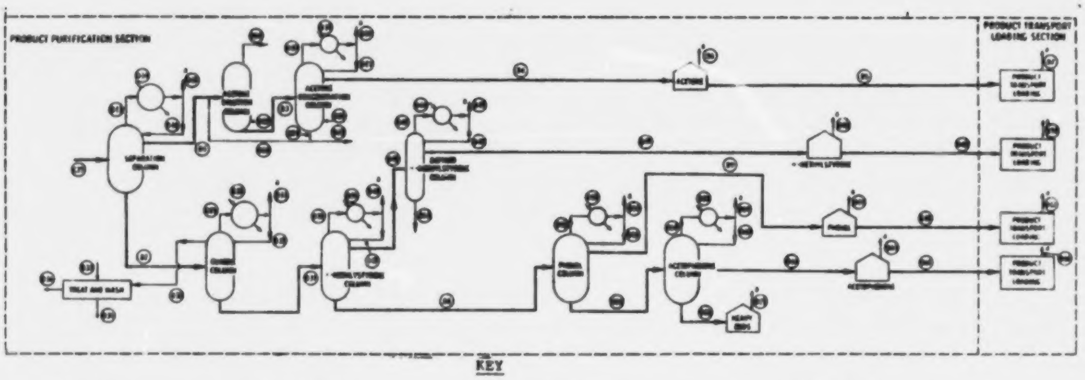
Acetone (Stream D4) is recovered and purified from the light ends fraction (Stream D1) by a dilution column and a concentration column. Wastes (Stream D23) are condensed and return to the process or otherwise disposed. Acetone (Stream D4) is removed from the acetone concentration column and the bottoms (Stream D26) are recycled (Stream D28) after excess water (Stream D27) is removed. The noncondensable vapors are vented to the atmosphere (Stream D20).

Cumene is recovered for recycle from the heavy fraction (Stream D2) in a cumene column. The noncondensable vapors are vented to the atmosphere (Stream D31). The cumene (Stream D33) is treated, washed, and recycled, generating treatment wastes (Stream D35).

The cumene column bottoms (Stream D37) are fed to an α-methylstyrene column. α-methylstyrene (Stream D42) is separated from a crude phenol stream (Stream D8). The noncondensable vapors (Stream D38) are vented to the atmosphere.

α-Methylstyrene is refined in another column, producing product (Stream D47), a stream recycled to the process (Stream D51), and noncondensable vapors (Stream D45) are vented to the atmosphere.

Phenol (Stream D9) is recovered from Stream D8 as the distillate of the phenol column. The noncondensable vapors (Stream D54) are vented to the atmosphere.


PRODUCT PURIFICATION SECTION
PRODUCT TRANSPORT LOADING SECTION
TREAT AND WASH
ACETONE
PHENOL
ACETOPHENONE
HEAVY ENDS

KEY

STREAM	IDENTIFICATION
C25	"WASHED PRODUCT STREAM
D1	LIGHT FRACTION
D2	HEAVY FRACTION
D3	CRUDE ACETONE
D4	REFINED ACETONE
D5	ACETONE
D6[a]	ACETONE STORAGE TANK EMISSIONS
D7[a]	ACETONE TRANSPORT LOADING EMISSIONS
D8	CRUDE PHENOL
D9	REFINED PHENOL
D10	PHENOL
D11[a]	PHENOL STORAGE TANK EMISSIONS
D12[a]	PHENOL TRANSPORT LOADING EMISSIONS
D13	VAPORS
D14	COOLING WATER
D15[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D16	RECYCLED CONDENSATE
D18	VAPORS
D19	COOLING WATER
D20[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D21	RECYCLED CONDENSATE
D22	HEAVY ENDS
D23[a]	HEAVY ENDS STORAGE TANK EMISSIONS
D24	WASTES
D25	STEAM
D26	BOTTOMS
D27	WATER
D28	RECYCLE
D29	VAPORS
D30	COOLING WATER
D31[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D32	RECYCLED CONDENSATE
D33	RECYCLE CUMENE
D34	TREATING AND WASHING STREAM
D35	TREATING AND WASHING WASTES
D36	RECYCLE CUMENE, TREATED AND WASHED
D37	PRODUCT STREAM
D38	VAPORS
D39	COOLING WATER
D40[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D41	RECYCLED CONDENSATE
D42	CRUDE α-METHYLSTYRENE
D43	VAPORS
D44	COOLING WATER
D45[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D46	RECYCLED CONDENSATE
D47	REFINED α-METHYLSTYRENE
D48	α-METHYLSTYRENE
D49[a]	α-METHYLSTYRENE STORAGE TANK EMISSIONS
D50[a]	α-METHYLSTYRENE TRANSPORT LOADING EMISSIONS
D51	RECYCLE
D52	VAPORS
D53	COOLING WATER
D54[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D55	RECYCLED CONDENSATE
D56	CRUDE ACETOPHENONE
D57	VAPORS
D58	COOLING WATER
D59[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D60	RECYCLED CONDENSATE
D61	REFINED ACETOPHENONE
D62	ACETOPHENONE
D63[a]	ACETOPHENONE STORAGE TANK EMISSIONS
D64[a]	ACETOPHENONE TRANSPORT LOAIDNG EMISSIONS

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[a] EMISSIONS TO ATMOSPHERE

Figure 9. Product purification section of the Allied process.

The bottoms (Stream D56) are fed to the acetophenone column, which produces acetophenone (Stream D61), a residue (heavy ends, Stream D22), and noncondensable vapors (Stream D59) which are vented to the atmosphere.

Hercules Process Technology--

Feed materials preparation--The feed materials required are cumene, air, buffer, and cleavage catalyst. Feed material streams are designated by the letter A before the stream number.

The cumene (Stream A2) must be at least 99.8% pure and may be obtained captively or on the open market (12, 14, 19, 20, and personal communication with L. B. Evans, 9 February 1976). If cumene is prepared captively, a purification step may be necessary. Such a step is considered to be part of the manufacture of cumene, not phenol.

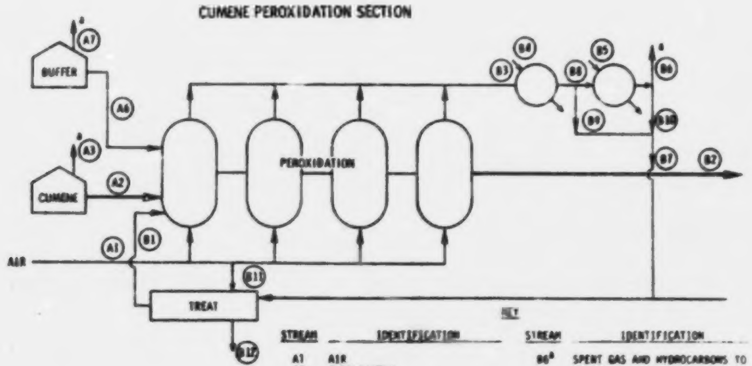
The air (Stream A1) is fed to the peroxidation vessels at approximately 620 kPa (personal communication with H. Walker, 7 October 1977). Air rather than oxygen is used because of economics (23).

The buffer, sodium carbonate (Na_2CO_3) is fed to the process in an aqueous solution (Stream A6).

The cleavage catalyst (Stream A4) is sulfuric acid. It is diluted before addition to the cleavage reactor with water, acetone, phenol, or another hydrocarbon or mixture of hydrocarbons (22).

Cumene peroxidation--Figure 10 shows this section of the Hercules process technology. Streams in this section are designated by the letter B before the stream number.

CUMENE PEROXIDATION SECTION



KEY

STREAM	IDENTIFICATION	STREAM	IDENTIFICATION
A1	AIR	B6[a]	SPENT GAS AND HYDROCARBONS TO AIR
A2	FEED CUMENE	B7	RECYCLE CUMENE
A3[a]	CUMENE STORAGE TANK EMISSIONS	B8	SPENT GAS AND NONCONDENSED
A6	BUFFER	B9	RECYCLE CUMENE
A7[a]	BUFFER STORAGE TANK EMISSION	B10	RECYCLE CUMENE
B1	RECYCLE CUMENE, TREATED	B11	TREATING STREAM
B2	CUMENE AND CUMENE HYDROPEROXIDE	B12	TREATING WASTES
B3	SPENT GAS		
B4	COOLING WATER		
B5	REFRIGERANT		

---

[a] EMISSION TO ATMOSPHERE.

Figure 10. Cumene peroxidation section of the Hercules process.

In the cumene peroxidation area, feed cumene, recycle cumene, air, and Na_2CO_3, a buffer, in aqueous solution (Streams A2, B1, A1, and A6) are fed to a vessel where cumene is peroxidized to cumene hydroperoxide in the liquid phase (7, 8, 14). The vessel is equipped for intimate gas-liquid contact, with the air stream providing the agitation. The vessel cooling system is necessary to control the temperature by removing the approximately 1,400 kJ/kg of cumene heat of reaction (which includes the contribution of side reactions) (7, 8, 12, 14).

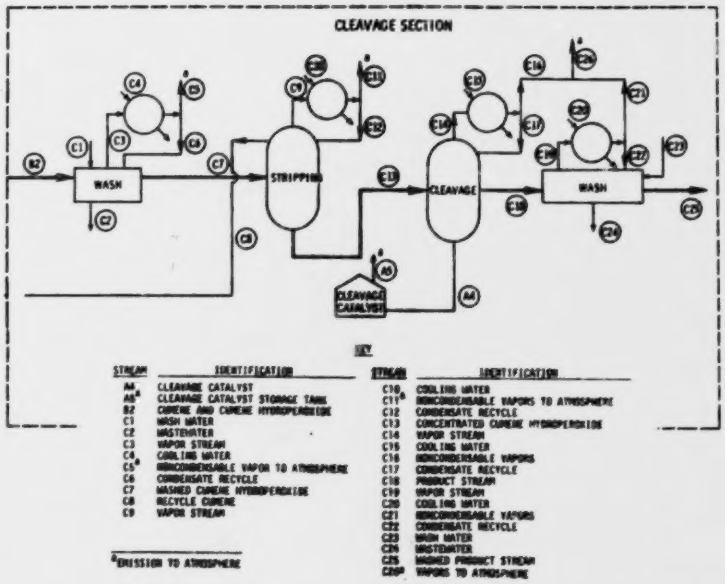
The air flow to the peroxidation step is at least 0.20 kg of air containing 21% oxygen per 1 kg of cumene fed (personal communication with L. B. Evans, 9 February 1976).

Present economics favor the use of air rather than oxygen; see the previous discussion in Section 3.A.3.a(2).

The operating temperatures range from 90°C to 120°C at pressures of approximately 620 kPa (personal communications with H. Walker, 7 October 1977, and with R. Canfield, 10 February 1978).

Entrained cumene, vaporized cumene, and vaporized hydrocarbons are recovered from the spent gas (Stream B3) by condensation, using cooling water and a refrigerant as heat transfer agents. The stream (B6) is released to the atmosphere.

Cleavage section--Figure 11 shows this section of the Hercules process technology. Streams in this section are designated by the letter C before the stream number.



KEY

STREAM	IDENTIFICATION
A4	CLEAVAGE CATALYST
A5[a]	CLEAVAGE CATALYST STORAGE TANK
B2	CUMENE AND CUMENE HYDROPEROXIDE
C1	WASH WATER
C2	WASTEWATER
C3	VAPOR STREAM
C4	COOLING WATER
C5[a]	NONCONDENSABLE VAPOR TO ATMOSPHERE
C6	CONDENSATE RECYCLE
C7	WASHED CUMENE HYDROPEROXIDE
C8	RECYCLE CUMENE
C9	VAPOR STREAM

STREAM	IDENTIFICATION
C10	COOLING WATER
C11[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
C12	CONDENSATE RECYCLE
C13	CONCENTRATED CUMENE HYDROPEROXIDE
C14	VAPOR STREAM
C15	COOLING WATER
C16	NONCONDENSABLE VAPORS
C17	CONDENSATE RECYCLE
C18	PRODUCT STREAM
C19	VAPOR STREAM
C20	COOLING WATER
C21	NONCONDENSABLE VAPORS
C22	CONDENSATE RECYCLE
C23	WASH WATER
C24	WASTEWATER
C25	WASHED PRODUCT STREAM
C26[a]	VAPORS TO ATMOSPHERE

[a] EMISSION TO ATMOSPHERE

Figure 11. Cleavage section of the Hercules process.

The cumene hydroperoxide stream (B2) is washed to remove the buffer and any water soluble material. The noncondensable vapors are vented (Stream C5) to the atmosphere. The wastewater (Stream C1) is sent to the process wastewater system.

The cumene hydroperoxide concentration area concentrates the relatively low cumene hydroperoxide concentration in the stream (Stream C7) from the wash operation to 80% by weight or higher (7, 8, 12, 15, and personal communication with H. Walker, 7 October 1977). Vacuum distillation or stripping is used to separate the cumene hydroperoxide (Stream C13) from the recycle cumene (Stream C8) which is treated before recycle. A thin or falling film evaporator may be used. The noncondensable vapors (Stream C11) are vented to the atmosphere.

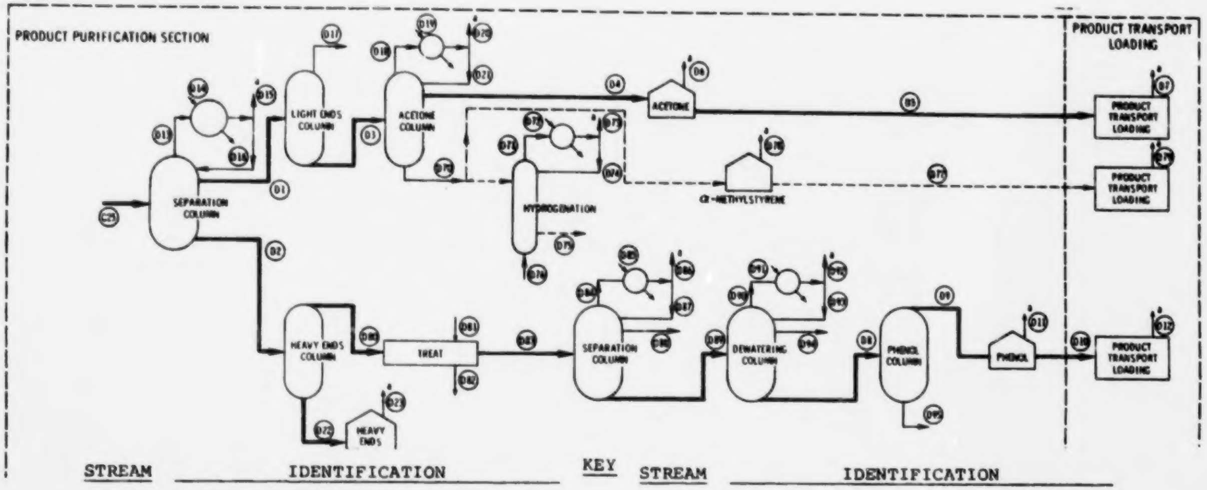
In the cleavage area, the concentrated cumene hydroperoxide (Stream C13) is cleaved to acetone and phenol in the presence of sulfuric acid (Stream A4) or other strong mineral acid. Concentrated cumene hydroperoxide is fed to a small, constant flow, stirred tank reactor along with sulfuric acid diluted to 5% to 10% by weight with acetone. Water, phenol or other hydrocarbons can be used for dilution (22). The liquid phase reaction is typically held at 50°C to 95°C at slightly elevated pressure, typically 136 kPa (4, 7, 8, 12, 13, 20-22). The reaction heat of approximately 1,500 kJ/kg cumene hydroperoxide boils approximately 1.26 kg acetone per 0.45 kg cumene hydroperoxide fed. The acetone stream (C6) is condensed and returned. The noncondensable vapors (Stream C5) are vented to the atmosphere (7, 8, 12, 13, 23).

The acid cleavage catalyst is removed by a water wash that contains a compound such as sodium sulfate, sodium phenolate, or other, to neutralize the acid (7, 8, 12, 13). The noncondensable vapors (Stream C21) are combined with those from the cleavage step (Stream C16) to be vented to the atmosphere (Stream C26). The wastewater (Stream C24) is sent to the process wastewater system.

Product purification--The product stream (C25) at this point contains phenol, acetone, cumene, acetophenone, α-methylstyrene, and other materials. The recovery and purification section consists of numerous columns. Streams in this section are designated by the letter D before the stream number.

Figure 12 shows this section of the Hercules process technology.

The products (Stream C25) are fed to a separation column which produces a light fraction (Stream D1) and a heavy fraction (Stream D2). The noncondensable vapors (Stream D15) are vented to the atmosphere.


PRODUCT PURIFICATION SECTION
PRODUCT TRANSPORT LOADING
SEPARATION COLUMN
LIGHT ENDS COLUMN
ACETONE COLUMN
ACETONE
HYDROGENATION
α-METHYLSTYRENE
PRODUCT TRANSPORT LOADING
PRODUCT TRANSPORT LOADING
HEAVY ENDS COLUMN
TREAT
HEAVY ENDS
SEPARATION COLUMN
DEWATERING COLUMN
PHENOL COLUMN
PHENOL
PRODUCT TRANSPORT LOADING
C25
D1
D2
D3
D4

KEY

STREAM	IDENTIFICATION	STREAM	IDENTIFICATION
C25	WASHED PRODUCT STREAM	D71	VAPORS
D1	LIGHT FRACTION	D72	COOLING WATER
D2	HEAVY FRACTION	D73[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D3	CRUDE ACETONE	D74	RECYCLED CONDENSATE
D4	REFINED ACETONE	D75	RECYCLE CUMENE
D5	ACETONE	D76	HYDROGEN
D6[a]	ACETONE STORAGE TANK EMISSION	D77	α-METHYLSTYRENE
D7[a]	ACETONE TRANSPORT LOADING	D78[a]	α-METHYLSTYRENE STORAGE TANK EMISSION
D8	CRUDE PHENOL	D79[a]	α-METHYLSTYRENE TRANSPORT LOADING EMISSION
D9	REFINED PHENOL	D80	MIDDLE FRACTION
D10	PHENOL	D81	TREAT STREAM
D11[a]	PHENOL STORAGE TANK EMISSION	D82	TREAT WASTES
D12[a]	PHENOL PRODUCT LOADING	D83	TREATED FRACTION
D13	VAPORS	D84	VAPORS
D14	COOLING WATER	D85	COOLING WATER
D15[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE	D86[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D16	RECYCLED CONDENSATE	D87	RECYCLED CONDENSATE
D17	LIGHT ENDS	D88	RECYCLE
D18	VAPORS	D89	CRUDE WET PHENOL
D19	COOLING WATER	D90	VAPORS
D20[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE	D91	COOLING WATER
D21	RECYCLED CONDENSATE	D92[a]	NONCONDENSABLE VAPORS TO ATMOSPHERE
D22	HEAVY ENDS	D93	RECYCLED CONDENSATE
D23[a]	HEAVY ENDS STORAGE TANK EMISSION	D94	WATER
D70	CRUDE α-METHYLSTYRENE	D95	RECYCLE

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[a] EMISSION TO ATMOSPHERE.

Figure 12. Product purification section of the Hercules process.

Acetone (Stream D4) is recovered and purified from the light ends fraction (Stream D1) by distillation in a light ends column and in an acetone column. The light ends (Stream D17) removed in the first distillation are condensed and returned to the process, or otherwise disposed, such as for use as fuel. Acetone (Stream D4) is distilled from the second column, and the bottoms (Stream D70) may be sold as crude α-methylstyrene, if the demand is present, or the stream can be hydrogenated to produce recycle cumene (Stream D75). If the crude α-methylstyrene is sold, the emissions are from storage tanks and product transport loading (Streams D78 and D79). If the crude α-methylstyrene is hydrogenated, the emissions are from the noncondensable vapors (Stream D73).

The heavy fraction (Stream D2) is separated into a middle fraction (Stream D80) and heavy ends (Stream D22). Acetophenone could be recovered from the heavy ends, but with the minor demand for it, it is not. The heavy ends may be sold, cracked, burned, or otherwise disposed of. The column is not vented. The middle fraction (Stream C80) is treated to remove impurities and fed to a separation column. The treatment wastes (Stream D82) are sent to the process wastewater system. A stream recycled to the process (Stream D88) is separated from the crude wet phenol (Stream D89). Noncondensable vapors (Stream D86) are vented to the atmosphere.

The crude wet phenol (Stream D89) is dewatered to produce a water stream (D94), crude phenol (Stream D8), and noncondensable vapors (Stream D92) which are vented to the atmosphere.

Phenol (Stream D9) and a stream recycled to the process (Stream D95) are produced from the phenol column.

Other Process Operations--

Waste disposal--Gaseous and liquid wastes are generated by the manufacture of acetone and phenol from cumene.

The gaseous wastes consist of light ends from acetone purification, and vapors. The light ends may be condensed and returned to the process, scrubbed and released to the atmosphere, released as is to the atmosphere, burned as fuel, or used in another process (personal communication with L. B. Evans, 9 February 1976). The vapors are hydrocarbons that were not condensed and were subsequently released to the atmosphere. The origins of these vapors were discussed in detail previously.

Liquid wastes include wastewater and heavy ends. The process wastewater system receives all wastewater and waste treatment streams and subsequently disposes of the wastes. A variety of methods, such as deep well injection, plant treatment systems, and municipal treatment systems, are used. Heavy ends are used as fuel, sold as a byproduct, cracked in a furnace, extracted, or used in another process (personal communication with L. B. Evans, 9 February 1976).

Tankage--The tankage requirements for a plant manufacturing acetone and phenol from cumene were estimated (see Appendix A) and are summarized in Table 6.

TABLE 6. TANKAGE REQUIREMENTS FOR A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE (136×10^3 metric tons/yr)

Composition	Number	Size, each m^3	Turnovers, each year	Temperature, °C
Phenol[a]	4	1,200	15	50 to 60
Acetone[b]	4	1,000	21	ambient
Cumene[b]	3	3,800	16	ambient
Acetophenone[a]	1	23	5	30
α-Methylstyrene[a]	1	95	27	30
Heavy ends[b]	1	190	102	70
Oxidation catalyst				
Cleavage catalyst				
Wastewater				

Note.—Blanks indicate no data available.

[a] Fixed roof tank, vents to atmosphere.

[b] Floating roof tank.

Product loading--Phenol, acetone, and the various byproducts are transported to the customer by railroad tank car, tanker truck, barge, or 0.21-m^3 drum.

Railroad tank cars, tanker trucks, barges, and drums are loaded by means of loading racks which meter and deliver the various materials from storage. The emission is caused by displacement of the vapors present in the item being filled. The vapors are a mixture of hydrocarbons and air. The hydrocarbon amounts depend on what was in the item previously, the material being loaded, and the method of filling (24).

Loading racks contain equipment to meter and deliver products into tank vehicles from storage either by overhead filling through the top hatch in the tank vehicle or by bottom filling at ground level. The elevated platform structure employed for overhead filling, constructed with hinged side platforms attached to the sides of a central walkway, can be raised when not in use. For loading, a tank vehicle is positioned adjacent to the central walkway and a hinged side platform is lowered to rest upon the top of the tank vehicle to access the top hatch. The meters, valves, loading tubes or spouts, motor switches, and similar necessary loading equipment are located on the central walkway. Bottom loading facilities are simpler since the tank vehicle is easily filled through accessible fittings on its underside.

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(24) Air Pollution Engineering Manual, Second Edition, J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

Loading of barges at modern terminals uses equipment similar to that used for elevated tank vehicle loading except for size. A pipeline manifold with flexible hoses is used for loading at older terminals. Marine installations are considerably larger and operate at much greater loading rates than inland loading facilities.

The loading arm assembly refers to the equipment at the discharge end of a product pipeline that is necessary for filling tank vehicles. Component parts include piping, valves, meters, swivel joints, fill spouts, and vapor collection adaptors.

Overhead loading arms can be pneumatic, counterweighted, or tension spring depending upon the manner in which the vertical movement of the arm is achieved. Bottom loading employs a flexible hose or a nonflexible, swing-type arm connected to the vehicle from the ground level storage facility.

Loading arms at modern marine terminals are similar in design to those used for overhead loading of tank vehicles. The barge loading arms are too large for manual operation, requiring a hydraulic system to effect arm motion. Older installations use reinforced flexible hoses to convey products from pipeline discharge manifolds to the barge. The hoses are positioned by means of a winch or crane (24).

Other process equipment--Hydrocarbon emissions other than from stacks and/or vents are considered fugitive. They occur from pressure relief valves, pump seals, compressor seals, pipeline valves and flanges, equipment purges, process drains, wastewater separators, and laboratory analysis sampling. Fugitive emissions may occur due to accidents, inadequate maintenance, or poor planning, although fugitive emissions occur even in the absence of such conditions and are unavoidable characteristics of some process operations.

Shutdowns and regenerations--Plants manufacturing phenol and acetone from cumene use continuous operations. Shutdowns, turnarounds, and startups to permit maintenance are scheduled. During this time equipment is purged of hydrocarbon vapors to allow maintenance access.

Ion exchange resin regeneration, which removes the acid cleavage catalyst, will contribute to wastewater streams.

Regeneration of carbon adsorption emission control equipment will also contribute to wastewater streams and vary the emission rate when the carbon bed is replaced on stream, if the system is in parallel. Also, the emissions will vary as the carbon bed becomes spent.

PLANT MATERIAL BALANCE

Figure 13 is a very simplified process diagram for the manufacture of acetone and phenol via cumene peroxidation. Table 7 contains an estimated material balance for a representative plant having 136×10^3 metric tons/yr phenol capacity utilized at 80%. The material balance was estimated using the product specifications in Appendix B, the emission information in Section 4, and stoichiometry.

GEOGRAPHIC DISTRIBUTION

Production of Phenol and Acetone

Phenol and acetone are produced by varied routes nationwide. Tables 8 and 9 list the companies, processes and capacities for phenol and acetone (2-4, 13, 25-33, and personal communication with L. A. Mattioli, 18 November 1976).

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(25) World Wide HPI Construction Boxscore. Hydrocarbon Processing, 54(2, Section 2):10, 1975.

(26) World Wide HPI Construction Boxscore. Hydrocarbon Processing, 55(2, Section 2):3, 9, 10, 14, 1976.

(27) World Wide HPI Construction Boxscore. Hydrocarbon Processing, 57(2, Section 2):4-19, 1978.

(28) Chem Sources U.S.A., 1976 Edition. Directories Publishing Company, Inc., Flemington, New Jersey, 1974. pp. 5, 6, 220, 519.

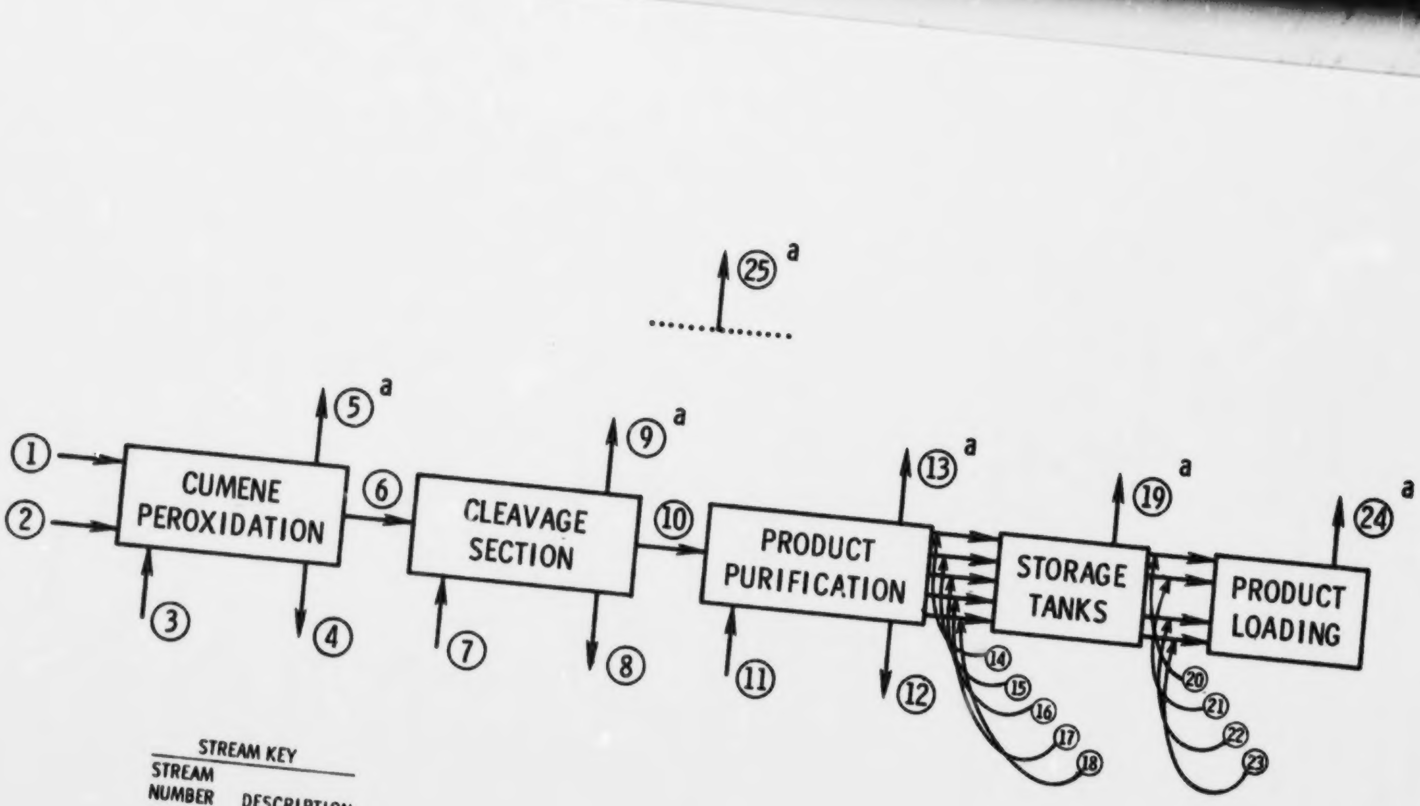
(29) 1978 Buyers' Guide Issue. Chemical Week, October 26, 1977, Part 2, pp. 306, 307, 415, 516, 523, 549, 568, 635.

(30) OPD Chemical Buyers Directory, 1977-1978. Schnell Publishing Company, New York, New York, 1977. pp. 23-24, 294, 556, 638.

(31) Preliminary Report on U.S. Production of Selected Synthetic Organic Chemicals, Preliminary Totals, 1976. S.O.C. Series C/P-77-1, United States International Trade Commission, Washington, D.C., 16 March 1977. 6 pp.

(32) Phenol Users Want to Be Phenol Makers. Chemical Week, 121(3):11-12, 1977.

(33) Phenol Producers Face Capacity Problems. Chemical and Engineering News, 55(30):8-9, 1977.


① ②
CUMENE PEROXIDATION
③ ④ ⑤ a
⑥
CLEAVAGE SECTION
⑦ ⑧ ⑨ a
⑩
PRODUCT PURIFICATION
⑪ ⑫ ⑬ a
⑭ ⑮ ⑯ ⑰ ⑱
STORAGE TANKS
⑲ a
⑳ ㉑ ㉒ ㉓
PRODUCT LOADING
㉔ a
㉕ a

STREAM KEY

STREAM NUMBER	DESCRIPTION
1	CUMENE
2	AIR
3, 7, 11	WATER
4, 8, 12	WASTEWATER
5	CUMENE PEROXIDATION EMISSIONS
6	CUMENE HYDROPEROXIDE
9	CLEAVAGE SECTION EMISSIONS
10	PRODUCT STREAM
13	PRODUCT PURIFICATION SECTION EMISSIONS
14, 20	PHENOL
15, 21	ACETONE
16, 22	ACETOPHENONE
17, 23	α -METHYLSTYRENE
18	HEAVY ENDS
19	STORAGE TANK EMISSIONS
24	PRODUCT TRANSPORT LOADING EMISSIONS
25	FUGITIVE EMISSIONS

a EMISSIONS

Figure 13. Simplified process flow diagram for the manufacture of acetone and phenol from cumene.

TABLE 7. ESTIMATED MATERIAL BALANCE FOR A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE (g/kg phenol produced)

Stream number:	1	2	3, 7, 11	4, 8, 12	5	6	9	10
Description:[a]	Cumene	Air	Water	Waste-water	Cumene peroxidation emissions	Cumene hydro-peroxide	Cleavage section emissions	Product stream
Component:[b]								
Phenol								--
Acetone					0.60		6×10^{-6}	--
Acetophenone					<0.0086		4.4×10^{-6}	--
α-Methylstyrene					<0.0001			--
Cumene	1,416.45				0.86	--	0.14	--
Cumene hydroperoxide						--		
Water			--	--				--
Nitrogen (N_2)		2,054			2,054			
Oxygen (O_2)		546.0			180			
Acetaldehyde								
Benzene					0.20		3.1×10^{-5}	
2-Butanone					0.050		1.8×10^{-6}	
2-Butenal					<0.0055		8.5×10^{-8}	
t-Butylbenzene	1.420				<0.0022		2.3×10^{-5}	
Dimethylstyrene					0.00005			
Ethylbenzene	1.420				0.00042		5.0×10^{-6}	
Formaldehyde					0.0010		$<2.6 \times 10^{-7}$	
2-Hydroxy-2-phenylpropane					<0.0009		3.4×10^{-6}	
Isopentanal							8.5×10^{-7}	
Mesityl oxide								
Naphthalene					<0.0001			
Propanal					<0.0011			
Hydrocarbons[c]	0.710			--		--		--
Total[d]	1,420	2,600	--	--	2,236	--	0.1401	--

Note.—Blanks indicate the component is not present; dashes indicate the quantity is unknown.

[a] Temperature and pressure are dependent upon the process technology used.

[b] Individual materials, especially those present in small amounts, will not balance due to information on the actual compounds listed as hydrocarbons not being known.

[c] Hydrocarbons in methane equivalents, based on carbon content, if known.

[d] Totals do not add due to rounding.

TABLE 7 (continued)

Stream number:	13	14, 20	15, 21	16, 22	17, 23	18	19	24	25
Description:[a]	Product purification section emissions	Phenol	Acetone	Aceto-phenone	α-Methyl-styrene	Heavy ends[e]	Storage tank emissions	Product transport loading emissions	Fugitive emissions
Component:[b]									
Phenol		999.75					0.051	0.11	
Acetone			608.45				0.060	0.074	
Acetophenone				1.078			5.5×10^{-5}		
α-Methylstyrene					21.18		0.0020		
Cumene					0.0427		0.028		
Cumene hydroperoxide									
Water		0.2000	1.831						
Nitrogen (N_2)									
Oxygen (O_2)									
Acetaldehyde					0.0002				
Benzene									
2-Butanone									
2-Butenal									
t-Butylbenzene									
Dimethylstyrene									
Ethylbenzene									
Formaldehyde									
2-Hydroxy-2-phenylpropane									
Isopentanal									
Mesityl oxide		0.0500							
Naphthalene									
Propanal									
Hydrocarbons[c]	1.20		0.0214	0.022	0.1071	--			0.0220
Total[d]	1.20	1,000	610.3	1.100	21.33	149.5	0.1411	0.184	0.0220

Note.—Blanks indicate the component is not present; dashes indicate the quantity is unknown.

[a] Temperature and pressure are dependent upon the process technology used.

[b] Individual materials, especially those present in small amounts, will not balance due to information on the actual compounds listed as hydrocarbons not being known.

[c] Hydrocarbons in methane equivalents, based on carbon content, if known.

[d] Totals do not add due to rounding.

[e] Hydrocarbon content of wastewater is not known. The amount is aggregated with the heavy ends so the total flow of hydrocarbons will balance. Hydrocarbons in methane equivalents based on carbon content if known.

TABLE 8. PHENOL PRODUCERS

Company and location	Process	Annual phenol capacity, 10^3 metric tons
Allied Chemical Corp. Frankford, PA	Allied cumene peroxidation.	272
Clark Oil and Refining Co. Blue Island, IL	Allied cumene peroxidation.	39
Dow Chemical Co.		
Midland, MI	Benzene chlorination.	18
Oyster Creek, TX	Allied cumene peroxidation.	180
Ferro Corp. Santa Fe Springs, CA	Natural.	–[a]
Georgia-Pacific Corp. Plaquemine, LA	Hercules cumene peroxidation.	120
Getty Oil Co. El Dorado, KS	Allied cumene peroxidation.	43
Kaiser Steel Fontana, CA	Natural.	–[a]
Kalama Chemicals Co. Kalama, WA	Toluene oxidation.	25
Koppers Co. Follansbee, WV	Natural.	–[a]
Merichem Co. Houston, TX	Natural.	–[a]
Monsanto Co. Chocolate Bayou, TX	Hercules cumene peroxidation.	227
Reichold Chemicals[b] Tuscaloosa, AL	Benzene sulfonation.	68
Shell Chemical Co. Deer Park, TX	Hercules cumene peroxidation	227
Sherwin-Williams –[a]	–[a]	–[a]
S.O. of Calif.: Chevron Richmond, CA	Hercules cumene peroxidation.	25
Stimson Lumber Co. Anacortes, WA	Natural.	–[a]
Union Carbide		
Bound Brook, NJ	Allied cumene peroxidation.	77
Marietta, OH	–[a]	–[a]
U.S. Steel Corp.		
Haverhill, OH	Hercules cumene peroxidation.	147
Clairton, PA	Natural.	–[a]
Total		1,468

[a] Not available.

[b] Production suspended in March 1978. Plant permanently closed December 1978.

TABLE 9. ACETONE PRODUCERS

Company and location	Raw material or process type	Annual capacity, 10^6 metric tons
Allied Chemical Corp Frankford, PA	cumene	0.15
Clark Oil and Refining Co. Blue Island, IL	cumene	0.02
Dixie Chemical Co. Bayport, TX	-[a]	-[a]
Dow Chemical Co. Oyster Creek, TX	cumene	0.13
Eastman Kodak Kingsport, TN	isopropanol	0.04
Exxon Corp. Bayway, NJ	isopropanol	0.06
Georgia-Pacific Corp. Plaquemine, LA	cumene	0.08
Getty Oil Co. El Dorado, KS	cumene	0.03
Goodyear Tire and Rubber Co. Bayport, TX	-[a]	-[a]
Monsanto Company Chocolate Bayou, TX	cumene	0.14
Oxirane Corp. Bayport, TX	propylene	0.03
Publicker Industries Philadelphia, PA	fermentation	stand-by
Shell Chemical Co.		
Deer Park, TX	cumene	0.14
Deer Park, TX	isopropanol	0.18
Dominquez, CA	isopropanol	0.05
Norco, LA	isopropanol	0.05
Skelly Oil Company El Dorado, KS	cumene	0.03
S.O. of California: Chevron Richmond, CA	cumene	0.01
Union Carbide		
Bound Brook, NJ	cumene	0.05
Institute and S. Charleston, WV	isopropanol	0.05
Texas City, TX	isopropanol	0.05
U.S. Steel Corp Haverhill, OH	cumene	0.09
Total		1.38

[a] Not available.

The area covered by this study does not include Puerto Rico. Whenever possible Puerto Rico's industry is not included in any calculations or tables.

Phenol is produced by 18 companies at 21 locations. The 1977 installed capacity for phenol production is 1,468 x 10^3 metric tons, of which approximately 93% or 1,358 x 10^3 metric tons is cumene based.

Acetone is produced by 17 companies at 22 locations. The cumene-based process accounts for approximately 60% or 831 x 10^3 metric tons of installed annual acetone capacity of 1,380 x 10^3 metric tons.

Location of Plants Manufacturing Acetone and Phenol from Cumene

There are currently 10 locations in the continental United States where phenol and acetone are produced from cumene (2, 3). They are listed in Table 10 by company. The locations are plotted in Figure 14.

Location of Cumene Producers

The 11 current producers of cumene in the continental United States (34) are listed in Table 11. Four of these manufacture acetone and phenol from cumene. All of the cumene production locations are indicated in Figure 14. Shell Chemical Company is planning construction of a 280 x 10^6 metric ton cumene plant (34).

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(34) Chemical Profile, Cumene. Chemical Marketing Reporter, 207(14):9, 1975.

TABLE 10. PLANTS MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Company[a]	Licenser	Phenol capacity, metric tons/yr
Allied Chemical Corp Specialty Chemicals Division Frankford, PA	Allied	272,000
Clark Oil and Refining Corp. Clark Chemical Corp. Blue Island, IL	Allied	39,000
Dow Chemical, U.S.A. Oyster Creek, TX	Allied	181,000
Georgia-Pacific Corp. Chemicals Division Plaquemine, LA	Hercules	120,000
Getty Oil Co. Getty Refining and Marketing Co. El Dorado, KS	Allied	43,000
Monsanto Company Monsanto Chemical Intermediates Chocolate Bayou, TX	Hercules	227,000
Shell Oil Co. Shell Chemical Co. Deer Park, TX	Hercules	227,000
S.O. of California Chevron Chemical Co. Richmond, CA	Hercules	25,000
Union Carbide Corp. Chemicals and Plastics Division Bound Brook, NJ	Allied	77,000
U.S. Steel Corp. Haverhill, OH	Hercules	147,000
Total		1,358,000

[a] Puerto Rico is not included in this study.

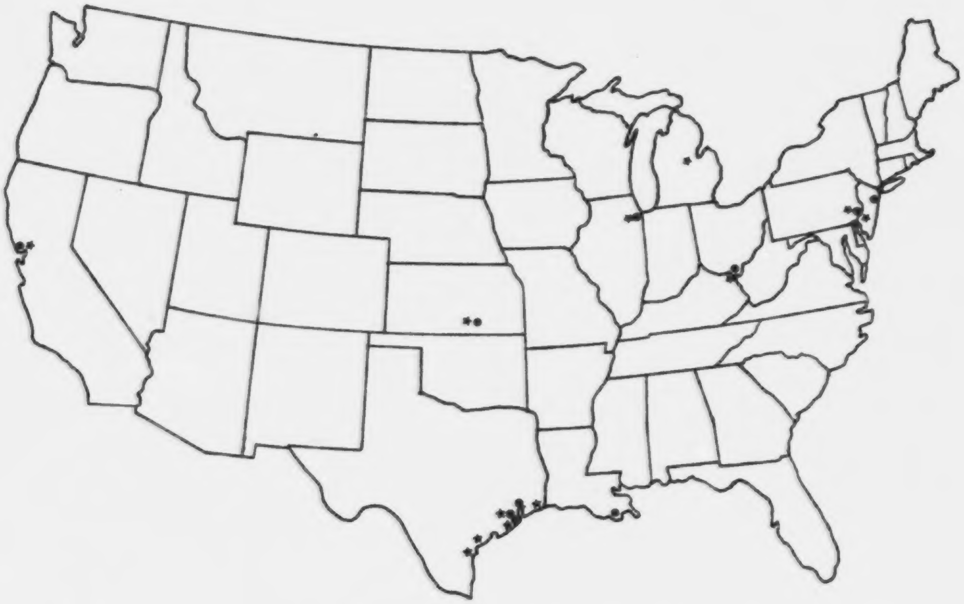

Figure 14. Locations of plants manufacturing phenol from cumene, and cumene.[a]

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[a] A • indicates a plant manufacturing acetone and phenol from cumene. A * indicates a plant manufacturing cumene.

TABLE 11. CUMENE PRODUCERS

Company and location	Annual cumene capacity, 10^6 metric tons
Ashland Oil, Inc.	
Ashland Chemical Co.	
Ashland, KY	0.148
Clark Oil and Refining Corp.	
Clark Chemical Corp.	
Blue Island, IL	0.054
Coastal States Gas Corp.	
Coastal States Marketing, Inc.	
Corpus Christi, TX	0.068
Dow Chemical Co.	
Midland, MI	0.005
Getty Oil Co.	
Getty Refining and Marketing Co.	
El Dorado, KS	0.068
Gulf Oil Corp.	
Gulf Oil Chemical Co.	
Philadelphia, PA	0.170
Port Arthur, TX	0.204
Marathon Oil Co.	
Texas City, TX	0.095
Monsanto Co.	
Monsanto Chemical Intermediates	
Chocolate Bayou, TX	0.306
S.O. of California	
Chevron Chemical Co.	
Richmond, CA	0.041
Sun Oil Co.	
Sun Oil Co. of PA	
Suntide Refining Co.	
Corpus Christi, TX	0.113
Texaco, Inc.	
Westville, NJ	0.068
Total	1.340

SECTION 4

EMISSIONS

In this section, air emissions are characterized by location, effective emission heights, and emission factors for criteria pollutants and selected pollutants; the hazard potential of each pollutant is quantified, and the affected population is determined; the national and state emission burdens are calculated; and the growth factor of the industry's emissions is determined. The data in this section were obtained through industry cooperation.

SELECTED POLLUTANTS

Compounds identified as potential emissions from the manufacture of acetone and phenol from cumene are listed in Table 12 (13, 14, and personal communication with L. B. Evans, 9 February 1976). A sampling program was undertaken to quantify these compounds plus others which may not previously have been known to be present. (See Appendices C through H.) Table 13 lists the materials identified during sampling plus those materials reported as emissions, along with the TLV's of the forms emitted, their primary ambient air quality standards where applicable, and their health effects (35-39).

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(35) TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1977. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1977. 94 pp.

(36) Air Quality Data - 1973 Annual Statistics. EPA-450/2-74-015, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1974. 151 pp.

(37) The Condensed Chemical Dictionary, Eighth Edition, G. G. Hawley, ed. Van Nostrand Reinhold Company, New York, New York, 1971. 971 pp.

(38) National Research Council. Vapor-Phase Organic Pollutants Volatile Hydrocarbons and Oxidation Products. EPA-600/1-75-005 (PB 249 357), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1975.

(39) Sax, N. I. Dangerous Properties of Industrial Materials. Van Nostrand Reinhold Company, New York, New York, 1975. 1258 pp.

TABLE 12. SUSPECTED EMISSIONS FROM ACETONE AND PHENOL MANUFACTURE FROM CUMENE PRIOR TO SAMPLING

Acetaldehyde
Acetic acid
Acetone
α-Hydroxyacetone
Diacetone alcohol
Acetophenone
Benzene
Ethylbenzene
n-Propylbenzene
Methyl isobutyl carbinol
Cumene
Cumene hydroperoxide
Dicumyl peroxide
1,1,2,2-Tetramethyl-1,2-diphenylethane
Formaldehyde
Formic acid
2-Methylbenzofuran
Methylgloxal
Heavy tars
2,6-Dimethyl-2,5-heptadiene-4-one
1-Hydroxyethyl methyl ketone
Methyl isobutyl ketone
Lactic acid
Mesityl oxide
Methanol
α-Methylstyrene
Dimers of α-methylstyrene
2-Methyl-3,4-pentanediol
4-Hydroxy-4-methyl-2-pentanone
Phenol
2,4,6-Tris(2-phenyl-2-propyl)phenol
2-Hydroxy-2-phenylpropane
2-Phenyl-2-(2-hydroxyphenyl)propane
2-Phenyl-2-(4-hydroxyphenyl)propane
Toluene

TABLE 13. CHARACTERISTICS OF EMISSIONS IDENTIFIED DURING SAMPLING OR REPORTED FROM ACETONE AND PHENOL PLANTS USING CUMENE PEROXIDATION

Material emitted	TLV, mg/m^3	Primary ambient air quality standard, g/m^3[a]	Health effects
Nonmethane hydrocarbons		0.000160 (3 hr)	
Acetaldehyde	180		Local irritant, central nervous system narcotic
Acetone	2,400		Skin irritant, narcotic in high concentrations
Acetophenone	-[b]		Narcotic in high concentrations
Benzene	30		Carcinogen
2-Butanone	590		Local irritant
2-Butenal	-[b]		Irritant, dangerous to eyes
t-Butylbenzene	-[b]		Details unknown
Cumene	245		Narcotic, toxic
Dimethylstyrene	-[b]		-[b]
Ethyl benzene	435		Skin and mucous membrane irritant
Formaldehyde	3		Irritant, toxic
Heavy ends	-[b]		-[b]
2-Hydroxy-2-phenylpropane	-[b]		-[b]
α-Methylstyrene	480		Toxic
Naphthalene	50		Moderate irritant
Phenol	19		Toxic, irritant
Propanal	-[b]		
Toluene	-[b]		Toxic
Arsenic	0.5		Toxic
Barium	0.5		Variable, depends on compound
Calcium	-[b]		Variable, depends on compound
Chlorine	3		Variable, depends on compound
Fluorine	2.5		Irritant, toxic
Magnesium	-[b]		Variable, depends on compound
Manganese	5		Variable, depends on compound
Phosphorus	-[b]		Variable, depends on compound
Potassium	-[b]		Variable, depends on compound
Sodium	-[b]		Variable, dependent on compound
Sulfur	-[b]		Variable, dependent on compound
Titanium	-[b]		Physiologically inert

Note.—Blanks indicate not applicable.

[a] There is no primary ambient air quality standard for hydrocarbons; the value used in this report is a guideline for meeting the primary ambient air quality standard for oxidants.

[b] Not available.

LOCATIONS AND DESCRIPTIONS

The process mechanism and the formation of atmospheric emissions were described in Section 3. Based on that information, the sources of emissions in a plant manufacturing acetone and phenol from cumene are listed in Table 14 for the two process technologies. Emissions for vents that are in closely related processing areas have been combined, resulting in the emission locations listed in Table 15. These emission locations apply to both process technologies used.

Average Emission Factors, Percent Error Bounds, and Methane Equivalent Emissions

Emission factors are defined to be grams of material emitted per kilogram of product produced. That is, for this report, emission factors are given in g/kg phenol produced.

Wherever possible emission factors are an average of several values for repeat measurements, and then for the two plants sampled. When this occurs the error bound, Σ, for the average, $\bar{x}$, of the emission factor is found as:

$$\Sigma = \frac{s \cdot t}{\sqrt{n}} \qquad (1)$$

where s = standard derivation of the emission factors
t = value from statistical tables for "Student t" distribution
n = number of items

The 95% confidence level and the degrees of freedom, f,

where

$$f = n - 1 \qquad (2)$$

are used to determine the value of t. Table 16 presents the t values for the 95% confidence level and various degrees of freedom. The 95% confidence level error bound is reported as a ± percent, ±%, determined by:

$$\pm\% = \frac{\Sigma}{\bar{x}} \qquad (3)$$

If the percentage determined is greater than 100, the minus value is reported only as 100 because negative emissions are physically impossible.

TABLE 14. EMISSION SOURCES BY PROCESS TYPE AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Process technology	Emission source
Allied	Cumene peroxidation.
	Cumene hydroperoxide concentration vent.
	Separation column vent.
	Acetone concentration column vent.
	Cumene column vent.
	α-Methylstyrene column vent.
	Refined α-methylstyrene column vent.
	Phenol column vent.
	Acetophenone column vent.
	Cumene tank vent.
	Acetone tank vent.
	α-Methylstyrene tank vent.
	Phenol tank vent.
	Acetophenone tank vent.
	Heavy ends tank vent.
	Catalyst tank vent.
	Acetone transport loading vent.
	α-Methylstyrene transport loading vent.
	Phenol transport loading vent.
	Acetophenone transport loading vent.
	Fugitive emissions.
Hercules	Cumene peroxidation vent.
	Cumene hydroperoxide wash vent.
	Cumene hydroperoxide concentration vent.
	Vent of cumene hydroperoxide cleavage and product wash operations combined.
	Separation column vent.
	Acetone column vent.
	Separation column vent.
	Dewatering column vent.
	Hydrogenation column vent.
	Acetone tank vent.
	α-Methylstyrene tank vent.
	Phenol tank vent.
	Heavy ends tank vent.
	Catalyst tank vent.
	Buffer tank vent.
	Acetone transport loading vent.
	α-Methylstyrene transport loading vent.
	Phenol transport loading vent.
	Fugitive emissions.

TABLE 15. EMISSION SOURCES AT A REPRESENTATIVE PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Emission sources
Cumene peroxidation vent
Cleavage section vents, combined
Product purification vents, combined
Storage tank vents, combined
Product transport loading vents, combined
Fugitive emissions

TABLE 16. VARIATION OF t WITH DEGREES OF FREEDOM FOR THE 95% CONFIDENCE LEVEL (40)

n	f[a]	t
2	1	12.706
3	2	4.303
4	4	3.182
5	4	2.776
6	5	2.571
7	6	2.447

[a] Assuming 1 mean.

The emission factors derived from the sampling program are the average of the emission factors for two plants. To determine the ± percent for the average emission factor, the root mean square of the error bounds for the two plants, A and B, is determined and changed to percent. The equation is:

$$\pm\% = \frac{\sqrt{\Sigma_A^{2} + \Sigma_B^{2}}}{\left(\dfrac{\bar{x}_A + \bar{x}_B}{2}\right)} 100 \qquad (4)$$

where $\Sigma = \dfrac{s \cdot t}{\sqrt{n}}$

and t is determined by the 95% confidence level and degrees of freedom.

The emission factor for total nonmethane hydrocarbons is not the sum of emission factors for all organic materials except methane. It is the sum of the methane equivalent emission factors for all organic materials except methane. The methane equivalent emission factor is based on the material emission factor and the carbon content. It is the amount of methane that would be emitted based on the carbon content of the material. A methane equivalent emission factor, MEEF, is calculated as:

$$\mathrm{MEEF} = \frac{E}{M_c} C_c M_m \qquad (5)$$

where E = material emission factor, g/kg phenol produced
M_c = material molecular weight, g/g mole
C_c = g moles of carbon that a gram mole of material contains
M_m = molecular weight of methane, 16.04 g/g mole

Cumene Peroxidation Vent

The cumene feed is contacted with air in a reaction vessel to peroxidize the cumene. Air is continuously introduced and removed. The off-gas stream carries vaporized hydrocarbons and some volatile trace elements. Cumene is recovered from the spent gas for recycle by condensation.

The emission control equipment is the last piece of equipment before the gas is emitted to the atmosphere. That is, any prior equipment is process equipment, and the control of any materials released to the atmosphere is performed by the last piece of equipment prior to release. For example, in the Allied process the emission control equipment is the carbon bed system, and in the Hercules process it is the refrigerated condenser, unless another piece of equipment is added on.

The average emission factors, determined by sampling at two plants and through industry cooperation, for the inlet and outlet of the control device are presented in Table 17. Only the inlet stream was sampled for trace elements. The control efficiency for cumene (which is 86% of the total nonmethane hydrocarbon emission, both calculated as equivalent methane) is 88%.

The emission factor for total nonmethane hydrocarbons as methane equivalents, based on carbon content, is 9.6 g/kg phenol produced for uncontrolled emissions and 1.2 g/kg phenol produced for controlled emissions. The average stack height is 17.1 m (56 ft).

Cleavage Section Vents, Combined

The composite emission factors, Table 18, are determined by aggregation of the emission factors available from sampling and industry communication. These emission factors combine values for the cumene hydroperoxide concentration vent (Allied process technology) and the cumene hydroperoxide wash vent, the cumene hydroperoxide concentration vent, and the combined cumene hydroperoxide cleavage and product wash vent (Hercules process technology).

TABLE 17. AVERAGE EMISSION FACTORS, UNCONTROLLED AND CONTROLLED, FROM THE PEROXIDATION VENT AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1977

Material emitted	Emission factor, g/kg phenol produced, ±95% confidence level bound[a,b] Inlet to control device	Outlet from control device
Criteria pollutants:[c]		
Total nonmethane hydrocarbons[d]	9.6	1.8
Chemical substances:		
Acetaldehyde	<0.0013 $^{+320\%}_{-100\%}$	<0.0021 $^{+320\%}_{-100\%}$
Acetone	2.4 $^{+840\%}_{-100\%}$	0.60 $^{+860\%}_{-100\%}$
Acetophenone	<0.0014	<0.0086
Benzene[e]	0.22 ± 16%	0.20 ± 9.4%
2-Butanone	0.089 $^{+200\%}_{-100\%}$	0.050 $^{+300\%}_{-100\%}$
2-Butenal	<0.0029 $^{+320\%}_{-100\%}$	<0.0055 $^{+460\%}_{-100\%}$
t-Butylbenzene	<0.0085	<0.0022
Cumene	6.9 $^{+240\%}_{-100\%}$	<0.86 $^{+170\%}_{-100\%}$
Dimethylstyrene	<0.0005	0.00005
Ethylbenzene	0.027	0.00042
Formaldehyde	0.038 $^{+460\%}_{-100\%}$	0.0010 $^{+520\%}_{-100\%}$
2-Hydroxy-2-phenylpropane	<0.0019	<0.0009
α-Methylstyrene[f]	<0.0005	<0.0001
Naphthalene	<0.0005	<0.0001
Propanal	<0.0017 $^{+220\%}_{-100\%}$	<0.0011 $^{+240\%}_{-100\%}$
Elements:		
Arsenic	<0.0000006 ± 71%[g]	-[h]
Barium	<0.0002 $^{+350\%}_{-100\%}$[i]	-[h]
Calcium	<0.0006 $^{+210\%}_{-100\%}$[i]	-[h]
Chlorine	<0.0002 $^{+400\%}_{-100\%}$[i]	-[h]
Fluorine	0.0002 $^{+400\%}_{-100\%}$[i]	-[h]
Magnesium	<0.00007 $^{+280\%}_{-100\%}$[i]	-[h]

(continued)

TABLE 17 (continued)

Material emitted	Emission factor, g/kg phenol produced, ±95% confidence level bound[a,b] Inlet to control device	 Outlet from control device
Manganese	0.000005 $^{+400\%}_{-100\%}$ [i]	-[h]
Phosphorus	<0.0002 $^{+400\%}_{-100\%}$ [i]	-[h]
Potassium	<0.0006 $^{+400\%}_{-100\%}$ [i]	-[h]
Sodium	<0.002 $^{+400\%}_{-100\%}$ [i]	-[h]
Sulfur	<0.0006 $^{+260\%}_{-100\%}$ [i]	-[h]
Titanium	<0.00005 $^{+340\%}_{-100\%}$ [i]	-[h]

Note.—Values given as less (<) are the amount in the sample only, because the amount in the in the blank was either greater than the amount in the sample, or not detected.

[a] The percent error bound for the average emission factor is the root mean square of the 95% confidence level error bounds at Plant A and Plant B. It is calculated by

$$\pm\% = \frac{\sqrt{\Sigma_A^2 + \Sigma_B^2}}{\left(\frac{\bar{x}_A + \bar{x}_B}{2}\right)} 100$$

and $\Sigma = \frac{s \cdot t}{\sqrt{n}}$

[b] Materials without the 95% confidence level error bound were tested once; therefore, no error bound can be determined.

[c] No particulates, nitrogen oxides (NO_x), sulfur oxides (SO_x), or carbon monoxide are emitted.

[d] The total nonmethane hydrocarbon emission factor is the sum of the methane equivalent emission factors, based on carbon content, for the C_2 through C_{16} materials determined by gas chromatographic (GC) analysis. The total nonmethane hydrocarbon emission factor is not the sum of emission factors for all nonmethane organic materials.

[e] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

[f] The GC/MS analysis does not distinguish among forms. It was assumed to be the α form.

[g] The error bound determined from the accuracy for atomic absorption (AA).

[h] Not sampled.

[i] The error bound determined from the accuracy for spark source mass spectrometry (SSMS).

TABLE 18. AVERAGE EMISSION FACTORS FOR THE CLEAVAGE SECTION VENTS COMBINED AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1976 and 1977

Material emitted	Emission factor, g/kg phenol produced[a]
Criteria pollutants:[b]	
Total nonmethane hydrocarbons[c]	0.17
Chemical substances:	
Acetone	0.0000060
Acetophenone	0.0000044
Benzene[d]	0.000031
2-Butanone	0.0000018
2-Butenal	0.000000085
t-Butylbenzene	0.000023
Cumene	0.14
Ethylbenzene	0.0000050
Formaldehyde	<0.00000026
2-Hydroxy-2-phenylpropane	0.0000034
Isopentanal	0.00000085

Note.—Values given as less than are the amount in the sample only, because the amount in the blank was either greater than the amount in the sample or not detected.

[a] Calculation of the 95% confidence level error bounds is not possible because some materials were tested once and because data obtained from industry and used to form the average emission factors do not have error bounds.

[b] No particulates, NO_x, SO_x, or carbon monoxide are emitted.

[c] The total nonmethane hydrocarbon emission factor is the sum of the methane equivalent emission factors, based on carbon content, for all nonmethane organic materials.

[d] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

Briefly, in the cleavage section the cumene hydroperoxide stream is washed (Hercules process only) and concentrated to 80% or more cumene hydroperoxide, the cumene removed is recycled, the cumene hydroperoxide is cleaved to products using an acid catalyst, and the catalyst is removed from the product stream. Section 3 has a more detailed description.

The total nonmethane hydrocarbon emission factor (as methane equivalents based on carbon content) is 0.17 g/kg phenol produced. The average stack height is 12.8 m (42 ft).

Product Purification Vents, Combined

The average emission factors, Table 19, for the product purification vents combined were determined from industry-supplied information. These emission factors combine the seven vents (Allied process technology) and the five vents (Hercules process technology) in this area. Briefly, the product purification section separates and purifies products and recycle streams. Section 3 describes this section in more detail.

TABLE 19. AVERAGE EMISSION FACTORS FOR THE PRODUCT PURIFICATION SECTION VENTS COMBINED AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1976

Material emitted	Emission factor, g/kg phenol produced, ±95% confidence level bound[a]
Criteria pollutants:[b]	
Total nonmethane hydrocarbons[c]	1.2 ± 53%
Chemical substances:	
Acetaldehyde	-[d]
Acetone	-[d]
Cumene	-[d]
α-Methylstyrene	-[d]
Phenol	-[d]

[a] The ± percent error bound determined using the 95% confidence level of the Student t distribution is found from:

$$\pm\% = \left(\frac{s \cdot t}{\sqrt{n}}\right)\left(\frac{1}{\bar{x}}\right)(100)$$

[b] No particulates, SO_x, NO_x, or carbon monoxide are emitted.

[c] The total nonmethane hydrocarbon emission factor is determined from the reported methane equivalent annual emissions.

[d] Qualitatively identified.

The total nonmethane hydrocarbon emission factor (as methane equivalents based on carbon content) is 1.2 g/kg phenol produced. The average stack height is 26.5 m.

Storage Tank Vents, Combined

The storage tank requirements for a representative plant producing acetone and phenol from cumene are listed in Table 6. Appendix A details the calculation procedures for estimating emission factors from tankage. The emission factor for the phenol tanks in an average of the calculated value 0.06 g phenol/kg phenol produced and an estimate of 0.012 g phenol/kg phenol produced supplied by H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 6 September 1978. H. Walker's phenol storage tank emission estimate was determined using the procedure described in Appendix A. However, based upon plant experience, he used other data for some of the input variables such as storage temperature, vapor pressure, etc. The two estimates were determined using the same procedure but different input variables; therefore, the estimates were averaged. The storage tank vent emission factors are listed in Table 20. The total nonmethane hydrocarbon emission factor for all storage tanks is 0.14 g nonmethane hydrocarbons/kg phenol produced. (The emission heights are discussed and listed later in Table 25.)

Product Transport Loading Vents, Combined

The emissions from product transport loading are caused by displacement of hydrocarbon-containing vapors in the compartment being filled. One source reports emissions of 0.061 g acetone/kg phenol produced from the acetone loading area and 0.20 g phenol/kg phenol produced from the phenol loading and shipping area. (Personal communication with Vernon C. Parker, Air Quality Section, Louisiana State Division of Health, New Orleans, Louisiana, 10 March 1976.) Another source estimates emissions from the phenol loading area as 0.010 g phenol/kg phenol produced. (Personal communication with H. Walker, Monsanto Chemical Intermediates, Alvin, Texas, 6 September 1978.) H. Walker's transport loading estimate is based on the working loss calculation from Appendix A for filling of based transport means such as barges. Plant experience provided data for the input variables. The two estimates were averaged. Table 21 lists the nonmethane hydrocarbon emission factor which is 0.17 g hydrocarbons/kg phenol produced, the acetone emission factor, and the phenol emission factor. The emission height was assumed to be 9.1 m.

Fugitive Emissions

Fugitive emissions occur from pressure relief valves, pump seals, compressor seals, pipeline valves and flanges, equipment purges, process drains, wastewater separators, and laboratory analysis sampling. An estimate of the total nonmethane hydrocarbons (as methane equivalents) from pumps and sewers has been reported to be 0.022 g/kg phenol produced in 1975 (personal communication with Vernon C. Parker, 10 March 1976). Pump and sewer caused fugitive emissions are not the total fugitive emissions, nor are they necessarily the most significant.

TABLE 20. CALCULATED EMISSION FACTORS FOR STORAGE TANK VENTS AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE

	Emission factor, g/kg phenol produced						
	Tanks[a]						
Material emitted	Acetone	Acetophenone	Cumene	Heavy ends	α-Methylstyrene	Phenol	Total
Criteria pollutants:[b]							
Total nonmethane hydrocarbons[c]	0.050	5.9×10^{-5}	0.034	0.011	0.0024	0.041	0.14
Chemical substances:[d]							
Acetone	0.060						0.060
Acetophenone		5.5×10^{-5}					5.5×10^{-5}
Cumene			0.028				0.028
α-Methylstyrene					0.0020		0.0020
Phenol				0.011[e]		0.040[f]	0.051

[a] There are 4 acetone, 1 acetophenone, 3 cumene, 1 heavy ends, 1 α-methylstyrene and 4 phenol tanks. Emission factors are for the appropriate number of tanks.

[b] No particulate, NO_x, SO_x, or carbon monoxide are emitted.

[c] The total nonmethane hydrocarbon emission factor is the sum of the methane equivalent emission factors, based on carbon content, for all organic materials except methane.

[d] Blanks indicate no emissions.

[e] Actual content of emission unknown. It was assumed to be phenol.

[f] The emission factor used is the average of a calculated value and an estimate supplied by H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 6 September 1978.

TABLE 21. REPORTED EMISSION FACTORS FOR PRODUCT TRANSPORT LOADING VENTS[a] COMBINED AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1975 AND 1978[b]

Material emitted	Emission factor, g/kg phenol produced
Criteria pollutants:[c]	
Total nonmethane hydrocarbons[d]	0.17
Chemical substances:	
Acetone	0.074
Phenol[e]	0.11

[a] Loading of 2 to 5 product types.

[b] Personal communication with Vernon C. Parker, Air Quality Section, Louisiana State Division of Health, New Orleans, Louisiana, 10 March 1976, and H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 6 September 1978.

[c] No particulate, NO_x, SO_x, or carbon monoxide are emitted.

[d] The total nonmethane hydrocarbon emission factor is the sum of the methane equivalent (based on carbon content) emission factors of the nonmethane organic materials.

[e] Average.

DEFINITION OF A REPRESENTATIVE SOURCE

A representative source was defined for plants manufacturing acetone and phenol from cumene to determine source severities for the emission points and compounds emitted. The data used to determine the representative source are presented in Table 22 (2, 3, 41, 42, and personal communication with L. B. Evans, 9 February 1976).

The representative source is a plant utilizing either technology licensed in the United States, and it has annual capacities of

- 136×10^3 metric tons of phenol
- 83×10^3 metric tons of acetone
- 2.9×10^3 metric tons of α-methylstyrene
- 150 metric tons of acetophenone

A capacity weighted mean county population of 1,333 persons/km^2 was used to calculate the affected population. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity, the population density may be lower or higher than the county average. The national average wind speed of 4.5 m/s is used as the wind speed for the representative source (42).

The representative source is utilized at 80% of capacity (0.8 stream-day factor), which reflects the industry-wide utilization of phenol from cumene plants (43).

The representative source utilizes the emissions control technologies listed in Table 23.

SOURCE SEVERITY

To assess the environmental impact of atmospheric emissions from plants manufacturing acetone and phenol from cumene, the source severity, S, for each material from each emission point was estimated. Source severity is defined as the pollutant concentration to which the population may be exposed divided by an

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(41) Chemical Profile, α-Methylstyrene. Chemical Marketing Reporter, 212(16):9, 1977.

(42) The World Almanac & Book of Facts, 1976; G. E..Delury, ed. Newspaper Enterprise Association, Inc., New York, New York, 1976. 984 pp.

(43) Capacity Use in Basic Chemicals Is Very Low. Chemical and Engineering News, 55(41):15-17, 1977.

TABLE 22. PLANT PARAMETERS USED IN DETERMINING THE REPRESENTATIVE SOURCE FOR A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Company and location[a]	Process type	Phenol capacity, 10^3 metric tons/yr	Acetone capacity, 10^3 metric tons/yr	Acetophenone capacity, metric tons/yr	α-Methylstyrene capacity,[b] 10^3 metric tons/yr	County	Population density, persons/km^2[c] (42)	Average wind speed m/s
Allied Chemical Corp. Frankford, Pa	Allied	272	150	-[d]	11	Philadelphia	5,836	-[e]
Clark Oil and Refining Corp. Blue Island, IL	Allied	39	24	910	2.3	Cook	2,224	-[e]
Dow Chemical Company Oyster Creek, TX	Hercules	181	127	0	0	Brazoria	29	-[e]
Georgia-Pacific Corp. Plaquemine, LA	Hercules	120	77	0	4.5	Iberville	19	-[e]
Getty Oil Company El Dorado, KS	Allied	43	26	181	0.91	Butler	10	-[e]
Monsanto Company Chocolate Bayou, TX	Hercules	227	136	0	0	Brazoria	29	-[e]
Shell Chemical Co. Deer Park, TX	Hercules	227	136	0	0	Harris	390	-[e]
S.O. of California Richmond, CA	Hercules	25	15	0	0	Contra Costa	292	-[e]
Union Carbide Corp. Bound Brook, NJ	Allied	77	49	-[d]	3.6	Somerset	249	-[e]
U.S. Steel Corp. Haverhill, OH	Hercules	147	51	0	6.8	Scioto	49	-[e]
			Representative plant					
Mean or parameter used	Either	136	83	150	2.9	-[f]	1,333[g]	4.5[e]
Percent error bounds[h]	-[f]	±46%	±44%	-[f]	±89%	-[f]	-[f]	-[f]

[a] Puerto Rico is not included in the area this study covers.

[b] Capacities are variable.

[c] Population density is determined on a county basis. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity, the population density may be lower or higher than the county average.

[d] Amount unknown.

[e] The national average wind speed of 4.5 m/s is used.

[f] Not applicable.

[g] The population density average is a capacity weighted mean county population density.

[h] The ± percent error bound was found using: $\pm\% = \left(\frac{s \cdot t}{\sqrt{n}}\right) \frac{1}{\bar{x}} 100$ where t is determined by the 95% confidence level of the Student t distribution and the degrees of freedom.

TABLE 23. EMISSION CONTROL TECHNOLOGIES USED AT REPRESENTATIVE PLANT

Emission source	Emission control technology
Cumene peroxidation vent	Adsorption or condensation
Cleavage section vents, combined	Condensation
Product purification vents, combined	Condensation
Storage tank vents:	
Acetone	Floating roof
Acetophenone	None
Cumene	Floating roof
Heavy ends	Floating roof
α-Methylstyrene	None
Phenol	None
Product transport loading vents, combined	Unknown
Fugitive	Not applicable

"acceptable concentration." The exposure concentration is the maximum time-averaged ground level concentration as determined by Gaussian plume dispersion methodology. The "acceptable contration" is that pollutant concentration at which an incipient adverse health reaction is assumed to occur. The "acceptable concentration" is defined as the corresponding primary ambient air quality standard for criteria pollutants and as a surrogate air quality standard for chemical substances determined by reducing threshold limit values (TLVs) using an appropriate safety factor. (See Appendix I for the complete derivation.) Source severity, S, is calculated as:

$$S = \frac{\overline{\chi}_{max}}{F} \qquad (6)$$

where $\overline{\chi}_{max}$ is the maximum time-averaged ground level concentration of each pollutant emitted from a representative plant, and F is defined as the primary ambient air quality standard for criteria pollutants (particulate, SO_x, NO_x, CO, and hydrocarbons[a]). For noncriteria pollutants, F is defined as:

$$F \equiv TLV \cdot 8/24 \cdot 0.01,\ g/m^3 = \frac{TLV}{300} \qquad (7)$$

The conversion factor, G = 1/300, converts the TLV to an "equivalent" primary ambient air quality standard. The factor 8/24 adjusts the TLV from an 8-hr work day to continuous (24-hr) exposure. The 1/100 factor is designed to account for the fact that the general population constitutes a higher risk group than healthy workers.

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[a] There is no primary ambient air quality standard for hydrocarbons; the value used in this report is a guideline for meeting the primary ambient air quality standard for oxidants.

Thus, the source severity represents the ratio of the exposure concentration to the acceptable concentration given pollutant.

The maximum ground-level concentration χ_{max}, is calculated according to Gaussian plume dispersion theory:

$$\chi_{max} = \frac{2\,Q}{\pi H^2 e \bar{u}} \tag{8}$$

where Q = mass emission rate, g/s
π = 3.14
$\bar{u}$ = average wind speed, m/s
H = effective emission height, m
e = 2.72

The effective emission height, H, is equal to the physical stack height, h', plus the amount of plume rise, ΔH. Plume rise in plants producing acetone and phenol from cumene represents less then 50% of the physical stack height as determined in Appendix L. See Appendix L for a determination of plume rise and its subsequent effect on the source severity.

The mass emission rate, Q in g/s, is calculated as:

$$Q = (E)(Cap)(U)k_1 \tag{9}$$

where E = emission factor, g/kg phenol produced
Cap = representative source phenol capacity, kg/yr
U = utilization
k_1 = conversion factor, yr/s

Equation 8 yields a value for a short-term averaging time during which the Gaussian plume dispersion equation is valid. The short-term averaging time was found to be 3 min in a study of published data on lateral and vertical diffusion. For a continuously emitting source, the time-averaged maximum ground level concentration for time intervals between 3 min and 24 hr can be estimated from the relation:

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t_1}\right)^{0.17} \tag{10}$$

where t_o = short-term averaging time (3 min)
t_1 = averaging time

The average emission factors for a plant manufacturing acetone and phenol from cumene were discussed previously and are summarized in Table 24. The average emission heights are presented in Table 25.

Table 26 lists the maximum time-averaged ground level concentration for each emission and each emission point in a representative plant.

Source severities for emissions which have TLVs or primary ambient air quality standards are listed by emission and emission point in Table 27 for a representative plant.

The largest source severity value listed in Table 27 is 3.5 for total nonmethane hydrocarbon emissions from the cumene perodixation vent.

The emissions from two emission points, the cumene peroxidation vent and the product purification vents, combined, represent 86% of the average emissions from a plant manufacturing acetone and phenol from cumene. Simulated source severity distributions, using methodology from Reference 44, for the total nonmethane hydrocarbon emissions (based on carbon content for methane equivalent) from those two points are presented in Figures 15 and 16. The simulated source severity distributions for the materials emitted from the cumene peroxidation vent are presented in Appendix J. The ordinate of the graph is interpreted as the percentage of plants manufacturing acetone and phenol from cumene having source severities less than the source severity value on the abscissa.

INDUSTRY CONTRIBUTION TO TOTAL ATMOSPHERIC EMISSIONS

Hydrocarbons (organic materials were classified as hydrocarbons) are the only criteria pollutant emitted by the manufacture of acetone and phenol from cumene, excluding emissions from boilers, which are assessed in a separate study.

The contribution from the manufacture of acetone and phenol from cumene to statewide and nationwide emissions was measured by the ratio of mass emissions from this source to total emissions from all stationary sources statewide and nationwide.

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(44) Eimutis, E. C., B. J. Holmes, and L. B. Mote. Source Assessment: Severity of Stationary Air Pollution Sources --A Simulation Approach. EPA-600/2-76-032e, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1976. 119 pp.

TABLE 24. AVERAGE EMISSION FACTORS FOR PHENOL AND ACETONE MANUFACTURE FROM CUMENE BY EMISSION POINT, 1977

Material emitted	Emission factor, g/kg of phenol produced Cumene peroxidation vent[a]	Cleavage section vents, combined[a,b,c]	Product purification vents, combined[d,e]
Criteria pollutants			
Total nonmethane hydrocarbons[f]	1.8	0.17	1.2 ± 53%[g]
Chemical substances:			
Acetaldehyde	<0.0021 + 320%[g] - 100%		-[h]
Acetone	0.60 + 860%[g] - 100%	0.0000060	-[h]
Acetophenone	<0.00086	0.0000044	
Benzene	0.20 ± 9.4%[g,i]	0.000031[i]	
2-Butanone	0.050 + 300%[g] - 100%	0.0000018	
2-Butenal	<0.0055 + 460%[g] - 100%	0.000000085	
t-Butylbenzene	<0.0022	0.000023	
Cumene	0.86 + 170%[g] - 100%	0.14	-[h]
Dimethylstyrene	0.00005		
Ethylbenzene	0.00042	0.00000050	
Formaldehyde	0.0010 + 520%[g] - 100%	<0.00000026	
2-Hydroxy-2-phenylpropane	<0.0009	0.0000034	
Isopentanal		0.00000085	
α-Methylstyrene	<0.0001[j]		-[h]
Naphthalene	<0.0001		
Phenol			-[h]
Propanal	<0.0011 + 240%[g] - 100%		

Note.—See footnotes at bottom of page 62.

(continued)

TABLE 24 (continued)

	Emission factor, g/kg of phenol produced					
	Storage tank vents[k,ℓ]					
Material emitted	Acetone tanks	Acetophenone tank	Cumene tanks	Heavy ends tank	α-Methylstyrene tank	Phenol[m] tanks
Criteria pollutants						
Total nonmethane hydrocarbons[f]	0.050	0.000059	0.034	0.011	0.0024	0.041
Chemical substances:						
Acetaldehyde						
Acetone	0.060					
Acetophenone		0.000055				
Benzene						
2-Butanone						
2-Butenal						
t-Butylbenzene						
Cumene			0.028			
Dimethylstyrene						
Ethylbenzene						
Formaldehyde						
2-Hydroxy-2-phenylpropane						
Isopentanal						
α-Methylstyrene					0.0020	
Naphthalene						
Phenol				0.011[n]		0.040
Propanal						

Note.—See footnotes at bottom of page 62.

(continued)

TABLE 24 (continued)

	Emission factor, g/kg of phenol produced		
Material emitted	Product transport loading vents, combined[o,p]	Fugitive emissions[q]	Totals
Criteria pollutants			
Total nonmethane hydrocarbons[f]	0.17	0.022	3.5
Chemical substances:			
Acetaldehyde			<0.0021
Acetone	0.074		0.73
Acetophenone			0.0087
Benzene			0.20
2-Butanone			0.050
2-Butenal			<0.0055
t-Butylbenzene			<0.0022
Cumene			1.0
Dimethylstyrene			0.000050
Ethylbenzene			0.00042
Formaldehyde			0.0010
2-Hydroxy-2-phenylpropane			<0.0009
Isopentanal			0.00000085
α-Methylstyrene			<0.0021
Naphthalene			<0.0001
Phenol	0.11[r]		0.16
Propanal			<0.0011

Note.—Blanks indicate no emissions for the sampled points and no emissions reported for the other sources. Values given as less than are the amount in the sample because the blank had either a greater amount than the sample or the material was not detected.

[a] Sampling performed.

[b] Emissions are from 1 to 4 vents.

[c] Data used are from 1976 and 1977.

[d] Emissions are from 5 to 7 vents.

[e] Data used are from industry sources for 1976.

[f] Emission factors for total nonmethane hydrocarbons do not equal the sum of all emission factors for all organic materials except methane. For the sampled emission points, to determine the total nonmethane hydrocarbon emission factor the methane equivalent emission factors, based on the carbon content, for the GC determinations of C_2 through C_{16} are calculated and summed. For reported emissions, the methane equivalent emission factors based on carbon content for all organic nonmethane materials are calculated and summed.

(continued)

TABLE 24 (continued)

[g] The percent error bounds are calculated using the Student t distribution to obtain:

$$\pm\% = \left(\frac{s \cdot t}{\sqrt{n}}\right)\frac{1}{x}\,100$$

[h] Qualitatively identified.

[i] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

[j] Assumed to be the α form. The GC/MS analysis does not distinquish among the forms.

[k] There were assumed to be 4 acetone, 1 acetophenone, 3 cumene, 1 heavy ends, 1 α-methylstyrene, and 4 phenol tanks.

[ℓ] Emission factors are calculated.

[m] The emission factor used is the average of a calculated value and an estimate supplied by H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 6 September 1978.

[n] Emissions assumed to be phenol.

[o] Loading of 2 to 5 product types.

[p] Data used are from industry sources for 1975 and 1978.

[q] Date used are from industry sources for 1975. The fugitive emissions estimate includes those from pumps and sewers only. The other sources of fugitive emissions are not included in this estimate.

[r] The emission factor is an average of two estimates.

TABLE 25. EMISSION HEIGHTS AT A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE[a]

Emission point	Emission height, m
Cumene peroxidation vent	17.1
Cleavage vents, combined	12.8
Product purification vents, combined	26.5
Storage tank vents:[b]	
Acetone	15.2
Acetophenone	4.6
Cumene	15.2
Heavy ends	9.1
α-Methylstyrene	6.1
Phenol	15.2
Product transport loading vents, combined[a]	9.1
Fugitive emissions[a]	4.6

[a] Plume rise represents less than 50% of the physical stack as determined in Appendix L. The physical stack height is used as the effective emission height. See Appendix L for determinating the plume rise correction and its subsequent effect on source severity.

[b] Estimated.

TABLE 26. MAXIMUM TIME-AVERAGED GROUND LEVEL CONCENTRATIONS OF ATMOSPHERIC EMISSIONS FROM A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1977

	$\bar{\chi}_{max}$, g/m^3		
Material emitted	Cumene peroxidation vent[a]	Cleavage section vents, combined[a,b,c]	Product purification vents, combined[d,e]
Criteria pollutants			
Total nonmethane hydrocarbons[f]	5.5×10^{-4}	9.3×10^{-5}	1.5×10^{-4}
Chemical substances:			
Acetaldehyde	$<4.5 \times 10^{-7}$		–[g]
Acetone	7.2×10^{-5}	1.3×10^{-9}	–[g]
Acetophenone	$<1.8 \times 10^{-6}$	1.7×10^{-9}	
Benzene	4.3×10^{-5}[h]	1.2×10^{-8}[h]	
2-Butanone	1.1×10^{-5}	6.9×10^{-10}	
2-Butenal	$<1.2 \times 10^{-6}$	3.3×10^{-11}	
t-Butylbenzene	$<4.7 \times 10^{-7}$	8.8×10^{-9}	
Cumene	1.8×10^{-4}	5.4×10^{-5}	–[g]
Dimethylstyrene	1.1×10^{-8}		
Ethylbenzene	9.0×10^{-8}	1.9×10^{-10}	
Formaldehyde	2.1×10^{-7}	$<1.0 \times 10^{-10}$	
2-Hydroxy-2-phenylpropane	$<1.9 \times 10^{-7}$	1.3×10^{-9}	
Isopentanal		3.3×10^{-10}	
α-Methylstyrene	$<2.1 \times 10^{-8}$[i]		–[g]
Naphthalene	$<2.1 \times 10^{-8}$		
Phenol			–[g]
Propanal	$<2.4 \times 10^{-7}$		

Note.—See footnotes at bottom of page 66.

(continued)

TABLE 26 (continued)

	$\bar{\chi}_{max}$, g/m^3					
	Storage tank vents[j,k]					
Material emitted	**Acetone tanks**	**Acetophenone tank**	**Cumene tanks**	**Heavy ends tank**	**α-Methylstyrene tank**	**Phenol tanks**[ℓ]
Criteria pollutants						
Total nonmethane hydrocarbons[f]	1.9×10^{-5}	2.5×10^{-7}	1.3×10^{-5}	1.2×10^{-5}	5.8×10^{-6}	1.6×10^{-5}
Chemical substances:						
Acetaldehyde						
Acetone	9.1×10^{-6}					
Acetophenone		1.7×10^{-7}				
Benzene						
2-Butanone						
2-Butenal						
_t_-Butylbenzene						
Cumene			7.6×10^{-6}			
Dimethylstyrene						
Ethylbenzene						
Formaldehyde						
2-Hydroxy-2-phenylpropane						
Isopentanal						
α-Methylstyrene					3.4×10^{-6}	
Naphthalene						
Phenol				8.3×10^{-6}[m]		1.1×10^{-5}
Propanal						

Note.—See footnotes at bottom of page 66.

(continued)

TABLE 26 (continued)

Material emitted	$\bar{x}_{max}$, g/m^3	
	Product transport loading facility vents[n,o]	Fugitive emissions[p]
Criteria pollutants		
Total nonmethane hydrocarbons[f]	1.8×10^{-4}	9.3×10^{-5}
Chemical substances:		
Acetaldehyde		
Acetone	3.1×10^{-5}	
Acetophenone		
Benzene		
2-Butanone		
2-Butenal		
t-Butylbenzene		
Cumene		
Dimethylstyrene		
Ethylbenzene		
Formaldehyde		
2-Hydroxy-2-phenylpropane		
Isopentanal		
α-Methylstyrene		
Naphthalene		
Phenol	8.3×10^{-5}[q]	
Propanal		

Note.—Blanks indicate no emissions for the sampled points and no emissions reported for the other sources.

[a] Sampling performed.

[b] Emissions are from 1 to 4 vents.

[c] Data used are from industry sources for 1976 and 1977.

[d] Emissions are from 5 to 7 vents.

[e] Data used are from industry sources for 1976.

[f] The maximum mean ground level concentrations for total nonmethane hydrocarbons do not equal the sum of the maximum mean ground level concentrations for all organic materials except methane.

[g] Qualitatively identified.

[h] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

[i] Assumed to be the α form. The GC/MS analysis does not distinguish among the forms.

[j] There were assumed to be 4 acetone, 1 acetophenone, 3 cumene, 1 heavy ends, 1 α-methylstyrene, and 4 phenol tanks.

[k] Emission factors are calculated.

[l] The emission factor used is the average of a calculated value and an estimate supplied by H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 6 September 1978.

[m] Emissions assumed to be phenol.

[n] Loading of 2 to 5 product types.

[o] Data used are from industry sources for 1975 and 1978.

[p] Data used are from industry sources for 1975. The fugitive emissions are those from pumps and sewers only. The fugitive emissions are not included in the estimate.

[q] The emission factor used is an average of two estimates.

TABLE 27. SOURCE SEVERITIES OF ATMOSPHERIC EMISSIONS FROM A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1977

	Source severity		
Material emitted	Cumene peroxidation vent[a]	Cleavage section vents, combined[a,b,c]	Product purification vents, combined[d,e]
Criteria pollutants			
Total nonmethane hydrocarbons[f]	3.5	0.58	0.96
Chemical substances:[g]			
Acetaldehyde	<0.00076		–[h]
Acetone	0.0090	1.6×10^{-7}	–[h]
Benzene	0.43[i]	1.2×10^{-5}[i]	
2-Butanone	0.0055	3.5×10^{-7}	
Cumene	0.23	0.066	–[h]
Ethylbenzene	0.000063	1.3×10^{-7}	
Formaldehyde	0.022	$<1.0 \times 10^{-5}$	
α-Methylstyrene	$<1.4 \times 10^{-5}$[j]		–[h]
Naphthalene	<0.00013		
Phenol			–[h]

Note.—See footnotes at bottom of page 69.

(continued)

TABLE 27 (continued)

Material emitted	Source severity Storage tank vents[k,ℓ] Acetone tanks	 Acetophenone tank	 Cumene tanks	 Heavy ends tank	 α-Methylstyrene tank	 Phenol tanks[m]
Criteria pollutants						
Total nonmethane hydrocarbons[f]	0.12	0.0016	0.082	0.074	0.036	0.10
Chemical substances:[g]						
Acetaldehyde						
Acetone	0.0011					
Benzene						
2-Butanone						
Cumene			0.0094			
Ethylbenzene						
Formaldehyde						
α-Methylstyrene					0.0021	
Naphthalene						
Phenol				0.13[n]		0.17

Note.—See footnotes at bottom of page 69.

(continued)

TABLE 27 (continued)

Material emitted	Source severity Product transport loading facility vents,[o,p]	 Fugitive emissions[q]
Criteria pollutants		
Total nonmethane hydrocarbons[f]	1.2	0.58
Chemical substances:[g]		
Acetaldehyde		
Acetone	0.0039	
Benzene		
2-Butanone		
Cumene		
Ethylbenzene		
Formaldehyde		
α-Methylstyrene		
Naphthalene		
Phenol	1.3[r]	

Note.—Blanks indicate no emissions for sampled points and no emissions reported for other sources.

[a] Sampling performed.

[b] Emissions are from 1 to 4 vents.

[c] Data used are from industry sources for 1976 and 1977.

[d] Emissions are from 5 to 7 vents.

[e] Data used are from industry sources for 1976.

[f] Source severity for total nonmethane organic materials will not equal the source severity for total nonmethane hydrocarbons. Source severities for the nonmethane organic materials are based on the toxicity of the chemicals. The source severity for total nonmethane hydrocarbons is based on the guideline for meeting the primary ambient air quality standard for photochemical oxidants.

[g] Only substances which have a TLV are listed.

[h] Qualitatively identified.

[i] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

[j] Assumed to be the α form. The GC/MS analysis does not distinguish among the forms.

[k] There were assumed to be 4 acetone, 1 acetophenone, 3 cumene, 1 heavy ends, 1 α-methylstyrene, and 4 phenol tanks.

[ℓ] Emission factors are calculated.

[m] The emission factor used is the average of a calculated value and an estimate supplied by H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 6 September 1978.

[n] Emissions assumed to be phenol.

[o] Loading of 2 to 5 product types.

[p] Data used are from industry sources for 1975 and 1978.

[q] Data used are from industry sources for 1975. The fugitive emissions are from pumps and sewers only. The other sources of fugitive emissions are not included in the estimate.

[r] The emission factor used is an average of two estimates.

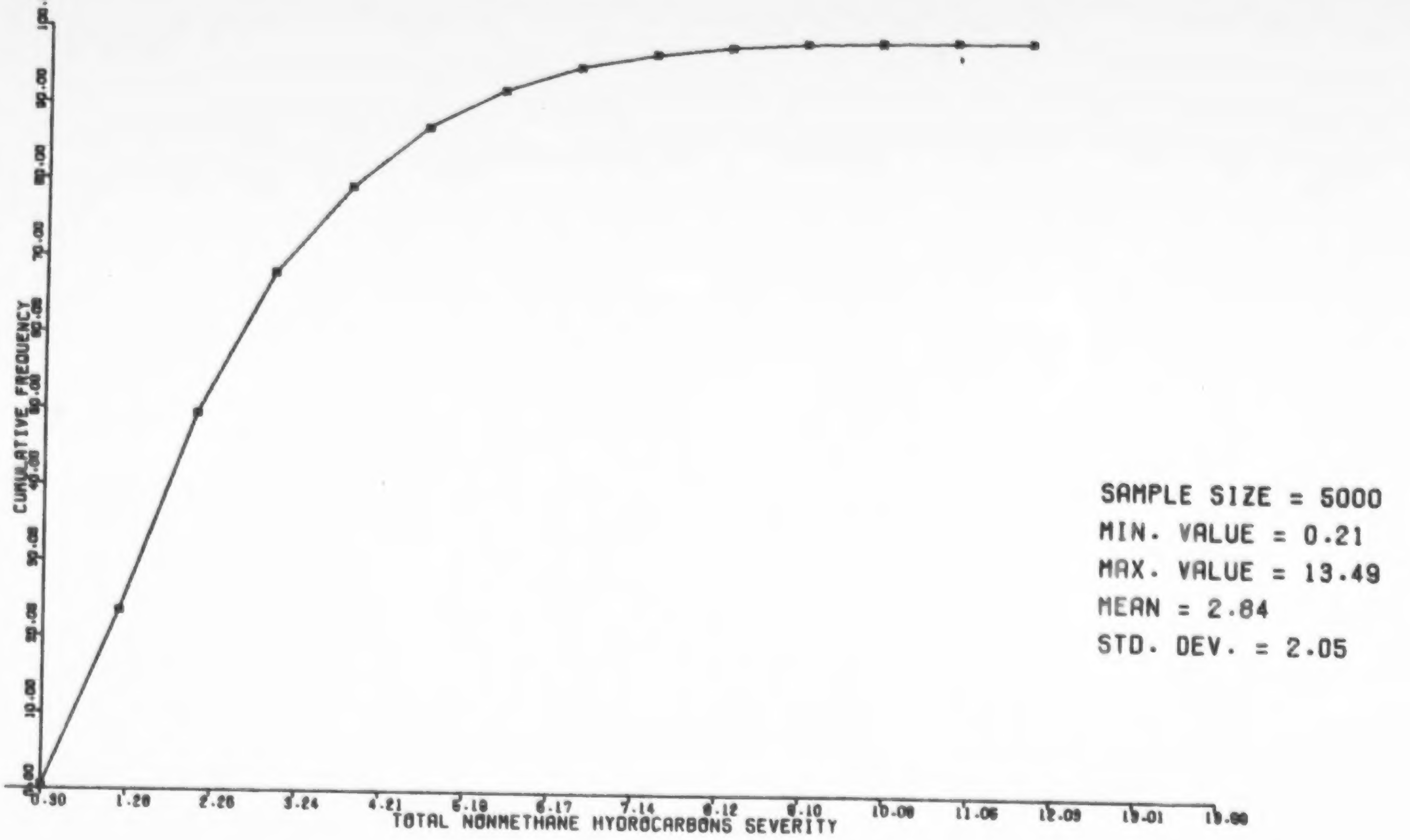

Figure 15. Simulated source severity distribution for total nonmethane hydrocarbons emitted from the cumene peroxidation vent.

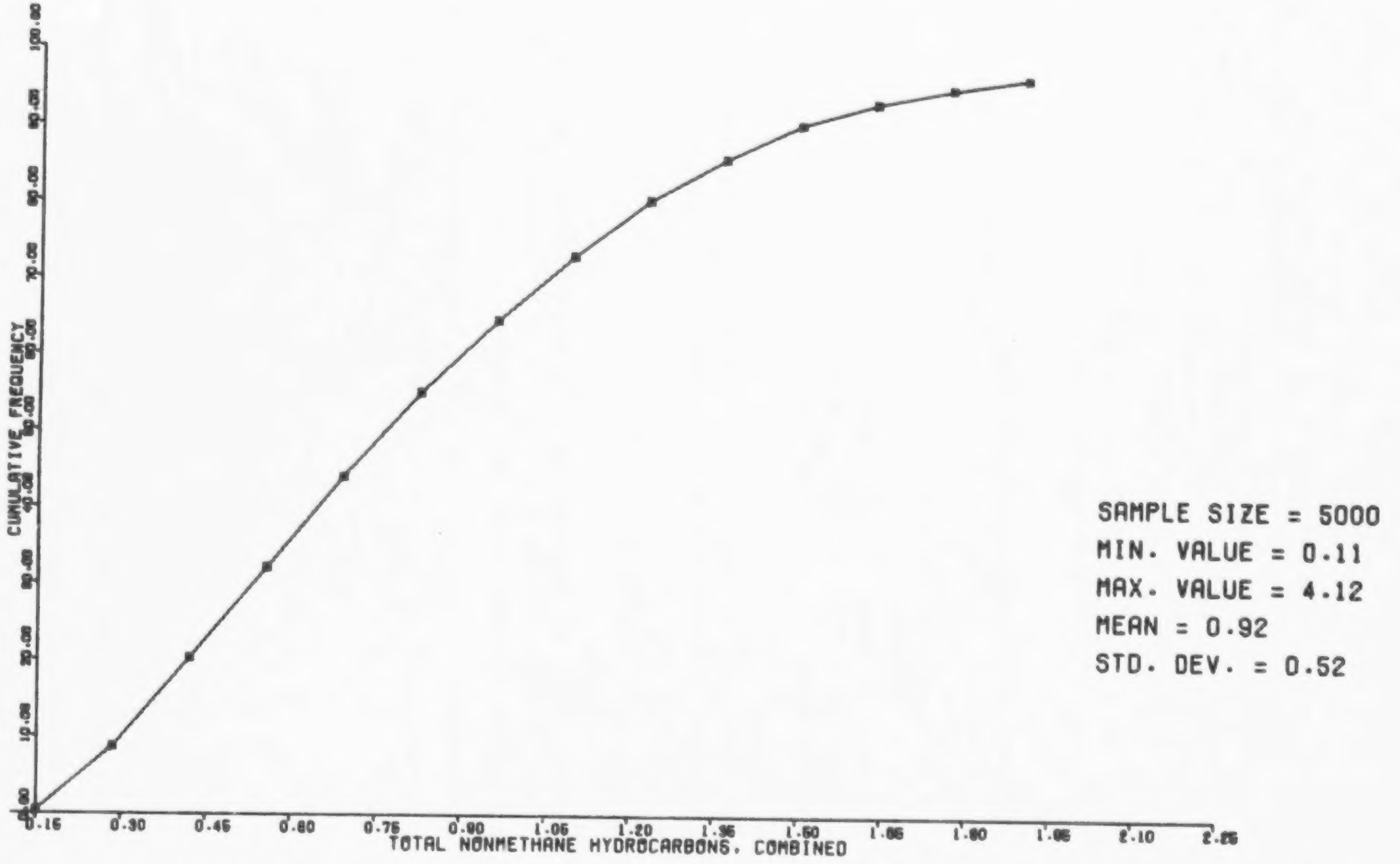

Figure 16. Simulated source severity distribution for total nonmethane hydrocarbons emitted from the product purification vents, combined.

The mass emissions of hydrocarbons resulting from acetone and phenol manufacture from cumene were calculated by multiplying the emission factor by the total production in each state and in the nation. The total production was calculated by multiplying the utilization factor by the total capacity in each state and in the nation. The total mass emissions from all stationary sources for each state and nationwide have been reported (45). The estimated contribution to total emissions of hydrocarbons (organic materials are classified as hydrocarbons) by the manufacture of acetone and phenol from cumene can be calculated using:

$$\%C = \left(\frac{EF_T \cdot U \cdot Cap_s \cdot k_4}{TE}\right) \cdot 100 \qquad (11)$$

where $\%C$ = percent estimated contribution

EF_T = total emission factor for nonmethane hydrocarbons, 3.5 g/kg phenol produced

Cap_s = total capacity on a state or national basis, metric tons/yr

k_4 = conversion factor, 10^{-3} kg/g

TE = total emissions of hydrocarbons from stationary source on a state or national basis, metric tons/yr

The mass emissions in each state and in the nation, the mass emissions from acetone and phenol production, and the percent contributions are shown in Table 28.

AFFECTED POPULATION

A measure of the population exposed to a high contaminant concentration due to a representative source producing acetone and phenol from cumene can be obtained as follows.

The value of the time-averaged ground level concentration, $\bar{\chi}$, as a function of the downwind dispersion distance from the source of emission release, x, can be determined from the equation (46):

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(45) Eimutis, E. C., and R. P. Quill. Source Assessment: State-by-State Listing of Criteria Pollutant Emissions. EPA-600/2-77-107b, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina, July 1977. 138 pp.

(46) Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11):859-863, 1972.

TABLE 28. ESTIMATED CONTRIBUTION TO TOTAL EMISSIONS OF HYDROCARBONS BY MANUFACTURE OF ACETONE AND PHENOL FROM CUMENE, 1977

Location[a]	1977 Total emissions of hydrocarbons,[b] 10^6 metric tons/yr	1977 Emissions from manufacture of acetone and phenol from cumene, metric tons/yr	Percent of total
Nationwide	16.58	3,800	0.023
California	1.423	70	0.0049
Illinois	0.8286	110	0.013
Kansas	0.2397	120	0.050
Louisiana	1.008	340	0.034
New Jersey	0.6341	220	0.034
Ohio	0.8387	410	0.049
Pennsylvania	0.9022	760	0.084
Texas	2.184	1,800	0.081

[a] Does not include Puerto Rico.

[b] Only hydrocarbons (organic materials were classified as hydrocarbons) are emitted by the manufacture of acetone and phenol from cumene, exclusive of boilers.

$$\overline{\chi}(x) = \frac{2.03\ Q}{\sigma_z \overline{u} x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \tag{12}$$

where Q = mass emission rate, g/s
H = effective emission height, m
x = downwind dispersion distance from the source of emission release, m
$\overline{u}$ = average wind speed (4.5 m/s)
σ_z = standard deviation of vertical dispersion, m

The effective emission height, H, is equal to the sum of the physical stack height plus the amount of plume rise, ΔH. The physical stack height has been used since plume rise amounts to only 50% of the physical stack height. See Appendix L for the determination of plume rise and its impact on dispersion calculations.

The values of x for which

$$\frac{\overline{\chi}(x)}{F} = 0.1 \tag{13}$$

are then determined by iteration.

For atmospheric stability, class C (neutral conditions), σ_z is given by (46):

$$\sigma_z = 0.113\ x^{0.911} \tag{14}$$

The affected area is then computed as:

$$A = \pi(x_2^2 - x_1^2),\ \text{km}^2 \tag{15}$$

where x_1 and x_2 are the two roots of Equation 12.

The affected area is computed based on the area outside the plant boundaries. The representative plant area is 2.9 km^2, thus in terms of the radial distance, x_1 must be at least 0.96 km. This value has been used to compute all affected areas and populations. If x_2 is not greater than 0.96 km, then all the affected area is inside plant boundaries and the affected area and population is reported as zero.

The capacity-weighted mean county population density, $\bar{D}_P$, is calculated as follows:

$$\bar{D}_P = \frac{\sum_i C_i D_{P_i}}{\sum_i C_i},\ \text{persons/km}^2 \tag{16}$$

where C_i = phenol production capacity of plant i, metric tons/yr

D_{P_i} = county population density for plant i, obtained from Reference 41, persons/km^2

Population density is determined on a county basis. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity, the population density may be lower or higher than the county average.

The product of A x $\bar{D}_P$ is designated the "affected population."

The affected population was computed for each compound and each emission point for which the source severity, S, exceeds 0.1. The results are presented in Table 29, where blank areas indicate the material shown is not discharged from the emission points listed; hence there is no affected population. Zeros indicate that the material is discharged from the emission point but that the resulting ambient levels have source severities less than or equal to 0.1, or that the affected area is entirely within the plant boundaries.

The total number of persons affected by a representative source manufacturing acetone and phenol from cumene is 12,600. This

TABLE 29. ESTIMATED AFFECTED POPULATION FROM MANUFACTURE OF ACETONE AND PHENOL FROM CUMENE AT REPRESENTATIVE SOURCE, 1977

	Affected population,[a,b,c] persons					
Component[d]	Cumene peroxidation vent	Cleavage section vents, combined[e]	Product purification vents, combined[f]	Storage tank vents, combined[g]	Product transport loading vents, combined[h]	Fugitive emissions
Total nonmethane hydrocarbons	8,300	0	4,300	0	0	0
Acetaldehyde	0		-[i]			-[j]
Acetone	0	0	-[i]	0	0	-[j]
Benzene	0	0				-[j]
2-Butanone	0	0				-[j]
Cumene	0	0	-[i]	0		-[j]
Ethylbenzene	0	0				-[j]
Formaldehyde	0	0				-[j]
α-Methylstyrene	0		-[i]	0		-[j]
Naphthalene	0					-[j]
Phenol			-[i]	0	0	-[j]

[a] Blank areas indicate that the material shown is not discharged from the emission point listed; zeros indicate that ambient levels resulting from discharged material produce source severiteries less than or equal to 0.1.

[b] The affected population is calculated for the affected area outside of the representative plant area, which is 2.9 km^2.

[c] The capacity weighted mean county population density is used to determine affected population. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity the population density may be lower or higher than the county average.

[d] Only materials which have TLV's or hazard factors are listed.

[e] Combination of 1 to 3 vents.

[f] Combination of 5 to 7 vents.

[g] There are 4 acetone, 1 acetophenone, 3 cumene, 1 heavy ends, 1 α-methylstyrene, and 4 phenol tanks. Affected population has been summed for all tanks.

[h] Loading of 2 to 5 product types.

[i] Emitted from this emission point, but no quantitative information is available.

[j] Unknown.

affected population represents the number of persons exposed to nonmethane hydrocarbons which exceed the one-tenth of the primary ambient air quality standard (guideline) for hydrocarbons of 160×10^{-6} g/m^3 (see Appendix K).

G. GROWTH FACTOR

In 1975, 703×10^3 metric tons of phenol were produced from cumene in the United States. As discussed in Section 6, production of phenol from cumene in 1980 is expected to reach $1{,}100 \times 10^3$ metric tons. Assuming that the same level of control technology exists in 1980 as existed in 1975, the emissions from the cumene peroxidation phenol industry will increase by 50% over that period; i.e.,

$$\frac{\text{Emissions in 1980}}{\text{Emissions in 1975}} = \frac{1{,}100 \times 10^3}{703 \times 10^3} = 1.56$$

SECTION 5

CONTROL TECHNOLOGY

Air emissions from the manufacture of acetone and phenol from cumene consist of hydrocarbons. Existing emission control technologies for the industry are described in this section. These control methods include condensation, absorption, adsorption, floating roof tanks, and incineration. Future considerations in emissions control technology are also discussed in this section.

INSTALLED EMISSIONS CONTROL TECHNOLOGY

Emission control technologies now being used in plants manufacturing acetone and phenol from cumene are listed in Table 30. The table lists the eight companies for which information was available. No information was available on the emission control equipment used by Shell Chemical Co., Deep Park, Texas, and Union Carbide Corp., Bound Brook, New Jersey. There are a variety of emission control methods used for each emission source. Table 31 lists the number of plants reporting the use of each emission control method for each emission source.

- Adsorption is the most commonly used method to control emissions from the cumene peroxidation vent. Condensation, absorption, and incineration are also used, however.

- Emissions in the cleavage section are most often controlled by condensation. Absorption and incineration are also used.

- Emissions in the product purification section are controlled by condensation, adsorption, absorption, and incineration.

- Floating roofs are used to control emissions from tanks, particularly acetone and cumene storage tanks. Condensation, sealed dome roofs, and conservation vents are also used for this purpose, but not as commonly as floating roofs.

- Product transport loading emissions are controlled by absorption or vapor recovery. Not all plants control this emission source.

- The scope of fugitive emissions and control methods are under study by EPA.

TABLE 30. INSTALLED EMISSIONS CONTROL TECHNOLOGY AT PLANTS MANUFACTURING ACETONE AND PHENOL FROM CUMENE

	Installed emission controls by company and location[a]	
Emission source	Allied Chemical Corp., Frankford, PA[b]	Clark Oil and Refining Corp., Blue Island, IL[c]
Cumene peroxidation vent	Carbon adsorbers.	Carbon adsorbers.
Cleavage section vents:		
Cumene hydroperoxide wash vent	Not applicable.	Not applicable.
Cumene hydroperoxide concentration vent	2 steam jets vented to brine cooled condenser.	To incinerator
Cumene hydroperoxide cleavage vent	Not applicable.	Not applicable.
Product wash vent	Not applicable.	Not applicable.
Product purification vents, combined	0-3 Steam Jet Condensers in series with final condenser vented to atmosphere. One steam jet condenser vented to packed water scrubber.	All to incinerator except two vents to carbon adsorbers.
Storage tank vents	2 acetone floating roof, 2 cumene floating roof. Miscellaneous additional to atmosphere.	2 acetone: floating roofs. 1 AMS: pressure vacuum vents 1 cumene: pressure vacuum vents. 2 phenol: none. 1 acetone: none. 1 AMS: none.
Product transport loading vents, combined	Vapor recovery system.	No control.
Fugitive emissions	Preventive maintenance program.	Not known.
Wastewater	Contaminated waste discharged to city treatment plant. Some streams discharged directly to waterway under NPDES permit.	Wastewater discharged to Metropolitan Sanitary District of Greater Chicago.

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[a] This study does not include Puerto Rico.

[b] Personal communication with M. W. Hunt, 10 April 1978.

[c] Personal communication with R. H. Bruggink, 5 May 1978.

(continued)

TABLE 30 (continued)

Emission source	Installed emission controls by company and location[a] Dow Chemical Co., Oyster Creek, TX[d]	Installed emission controls by company and location[a] Georgia-Pacific Corp., Placquemine, LA[e]
Cumene peroxidation vent	Carbon adsorber and thermal incinerator.	Carbon bed system.
Cleavage section vents:		
Cumene hydroperoxide wash vent	Not applicable.	Not applicable.
Cumene hydroperoxide concentration vent	Not available.	Condenser.
Cumene hydroperoxide cleavage vent	Not applicable.	Condenser.
Product wash vent	Not applicable.	Not applicable.
Product purification vents, combined	Not available.	Acetone topping column condenser; acetone column condenser; AMS tower incineration.
Storage tank vents	2 cumene: floating roof 4 phenol: none. 4 acetone: none. 1 cumene: none.	1 phenol and acetone: water cooled condenser 1 phenol and heavy ends: none. 2 heavy ends: none. 2 phenol: none. 2 acetone: none. 3 AMS: none 2 cumene: conservation vent. 2 acetone: vent condenser. 2 phenol: conservation vent. 1 oxidate surge tank: none
Product transport loading vents, combined	Not available.	None.
Fugitive emissions	Not available.	Not available.
Wastewater	Deep well injection.	Treatment system.

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[a] This study does not include Puerto Rico.

[d] Personal communication with L. B. Evans, 9 February 1976.

[e] Personal communication with J. J. Davies, 22 May 1978.

(continued)

TABLE 30 (continued)

Emission source	Installed emission controls by company and location[a]	
	Getty Oil Co., El Dorado, KS[f]	Monsanto Co., Chocolate Bayou, TX[g]
Cumene peroxidation vent	Cumene recovery system including carbon adsorption.	Cooling water condenser, demister separator, refrigerated condenser, demister-separator.
Cleavage section vents:		
Cumene hydroperoxide wash vent	Not applicable.	Condenser.
Cumene hydroperoxide concentration vent	Steam jet vent to atmosphere.	Condenser
Cumene hydroperoxide cleavage vent	Not applicable.	Condenser and no control.
Product wash vent	Not applicable.	
Product purification vents, combined	3 vents to atmosphere; 5 steam jet vents to atmsophere.	Vent condensers and incinerators.
Storage tank vents	2 cumene: none. 1 raw products: none. 1 refined AMS: none. 2 acetone: none and floating roof. 2 phenol: none. 1 crude AMS: none. 1 waste oils: none. 3 wastewater: none.	Not available.
Product transport loading vents, combined	No control.	Not available.
Fugitive emissions	Preventative maintenance.	Not available.
Wastewater	Refinery treatment system.	Deep well injection.

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[a] This study does not include Puerto Rico.

[f] Personal communication with R. G. Soehlke, 16 May 1978.

[g] Personal communication with H. Keating, 20 January 1978.

(continued)

TABLE 30 (continued)

Emission source	Installed emission controls by company and location[a] Standard Oil of California Richmond, CA[h]	 U.S. Steel Corp., Haverhill, OH[i]
Cumene peroxidation vent	Vapor scrubber and condenser.	Cooling water condenser, demister-separator, NH_3 condenser, demister separator.
Cleavage section vents:		
Cumene hydroperoxide wash vent	Not applicable.	Not applicable.
Cumene hydroperoxide concentration vent	Vapor condenser.	Not applicable.
Cumene hydroperoxide cleavage vent	Vapor condenser.	Tank vent with cooling water condenser.
Product wash vent	Scrubber.	
Product purification vents, combined	Separation: vapor condenser. Acetone column I: scrubber. Acetone column II: vapor condenser. Phenol recovery: vapor condenser.	Thru CW and NH_3 vent condensers and conservation vents to Atm.
Storage tank vents	5 cumene: floating roof 1 cumene and CHP: floating roof. 1 acetone and phenol: dome roof, sealed. 6 acetone: dome roof, sealed. 7 phenol: dome roof, sealed. 2 residual oil: floating roof. Na_2CO_3 in H_2O: cone roof with vent.	Crude AMS: none Cumene: conservation vent. Phenol: conservation vent. Acetone: 2 floating roofs and 1 cooling water condenser. Heavy hydrocarbons: cooling water condenser.
Product transport loading vents, combined	Scrubber on tank truck loading.	No control.
Fugitive emissions	Double seals on pumps.	Minor - no estimate.
Wastewater	Refinery treatment system.	Deep well injection.

[a] This study does not include Puerto Rico.

[h] Personal communication with J. Blickman, 27 April 1978.

[i] Personal communication with C. Parris, 4 April 1978.

TABLE 31. NUMBER OF PLANTS REPORTING USAGE OF EMISSION CONTROL METHODS IN INDICATED SECTION OF THE PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE

	Number of plant reporting usage of control method for each emission location									
Emission source	Condensation	Adsorption	Absorption (scrubbing)	Incineration	Floating roof tank	Sealed dome roof tank	Conservation vent on tanks	Vapor recovery on loading	Other	No control
Cumene peroxidation vent	3	5	1	1	-[a]	-	-	-	0[b]	0
Cleavage section vents, combined[c]	5	0	1	1	-	-	-	-	0	2
Product purification vents, combined[d]	5	1	2	3	-	-	-	-	0	0
Storage tank vents, combined[e]	2	0	0	0	5	1	3	0	0	6
Product transport loading vents, combined[f]	0	0	1	0	-	-	-	1	0	3
Fugitive emissions	-	-	-	-	-	-	-	-	-[g]	0

[a] Dashes indicate control method not applicable to emission source such as floating roof tank for the cumene peroxidation vent.

[b] Zeros indicate control suitable for emission source but no reported use.

[c] There are 1 to 4 vents.

[d] There are 5 to 7 vents.

[e] There are various numbers of tanks.

[f] There are 2 to 5 products.

[g] Not known; preventive maintenance programs; double seals on pumps; minor emissions.

The following subsection briefly describes the emission control methods reported in use at cumene peroxidation plants.

Vapor Condensation

Organic compounds can be removed from an air stream by condensation. A vapor will condense when, at a given temperature, the partial pressure of the compound is equal to or greater than its vapor pressure. Similarly, if the temperature of a gaseous mixture is reduced to the saturation temperature (i.e., the temperature at which the vapor pressure equals the partial pressure of one of the constituents), the material will condense. Thus, either increasing the system pressure or lowering the temperature can cause condensation (47). In most air pollution control applications, decreased temperature is used to condense organic materials, since increased pressure is usually impractical (48).

Equilibrium partial pressure limits the control of organic emissions by condensation. As condensation occurs, the partial pressure of material remaining in the gas decreases rapidly, preventing complete condensation (48).

Figure 17 illustrates the effects of temperature and pressure on equilibrium cumene concentration in a gaseous stream. Under isobaric conditions, the concentration of cumene is directly proportional to its vapor pressure (49). Table 32 gives some examples of the amount of cumene contained in a saturated gas stream at various temperatures and pressures. These temperatures are typical of the exit gas temperatures from cooling water and refrigerated condensers.

One system employing condensation for emission control on the cumene peroxidation vent is shown in Figure 18. Table 33 presents the material balance for this system. The stream components were determined by material balance calculations performed by industry (personal communication with L. B. Evans, 9 February 1976).

This system sends the off-gas (Stream A) from the cumene peroxidation reactor through a cooling water condenser, separates the liquid and gaseous streams, and sends the gaseous stream through

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(47) Control Techniques for Hydrocarbons and Organic Solvent Emissions from Stationary Sources. Publication No. AP-68, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, March 1970. 114 pp.

(48) Hydrocarbon Pollutant Systems Study, Volume I: Stationary Sources, Effects and Control. EPA 71-12 (PB 219 073), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 20 October 1972. 377 pp.

(49) Jordan, T. E. Vapor Pressures of Organic Compounds. Interscience Publishers, Inc., New York, New York, 1954.

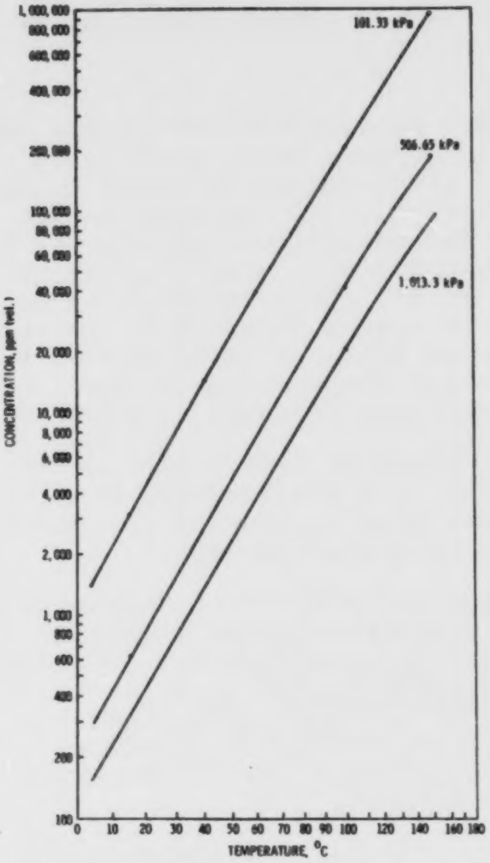

Figure 17. Variation of cumene concentration with temperature and pressure.

TABLE 32. AMOUNT OF CUMENE IN A SATURATED GAS STREAM AT VARIOUS CONDITIONS

Pressure, kPa	Temperature, °C	Cumene, ppm by volume
101	15	3,100
101	4	1,400
1,010	15	310
1,010	4	140

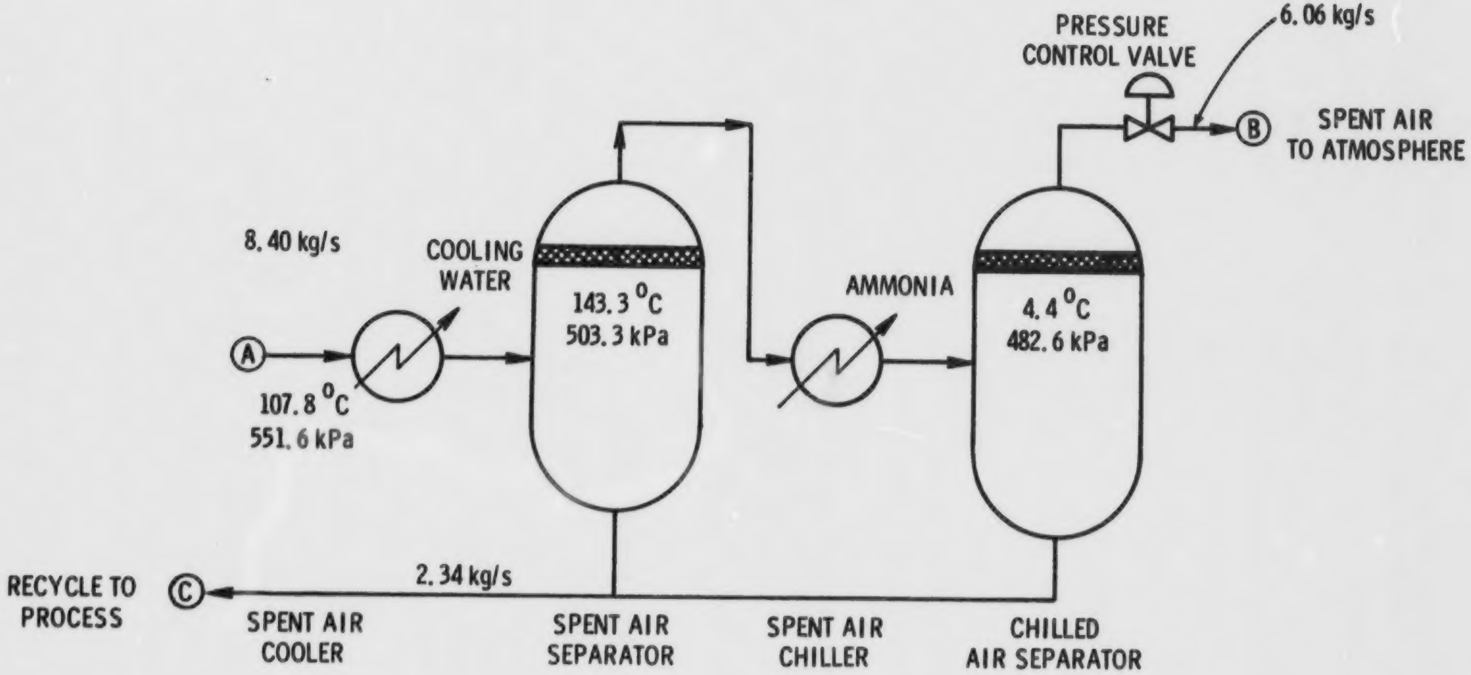
PRESSURE CONTROL VALVE
6.06 kg/s
Ⓑ
SPENT AIR TO ATMOSPHERE
8.40 kg/s
COOLING WATER
Ⓐ
107.8 °C
551.6 kPa
143.3 °C
503.3 kPa
AMMONIA
4.4 °C
482.6 kPa
RECYCLE TO PROCESS
Ⓒ
2.34 kg/s
SPENT AIR COOLER
SPENT AIR SEPARATOR
SPENT AIR CHILLER
CHILLED AIR SEPARATOR

Figure 18. Condensation used as emission control on the cumene peroxidation vent.[a]

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[a] Personal communication with L. B. Evans, 9 February 1976.

TABLE 33. MATERIAL BALANCE FOR AN EMISSION CONTROL SYSTEM ON THE CUMENE PEROXIDATION VENT USING CONDENSATION[a]

	In	Out	
Component	Stream A, kg/s	Stream B, kg/s	Stream C, kg/s
O_2	0.44	0.44	0
N_2	5.61	5.61	0
Cumene	1.275	0.005	1.270
Acetophenone	0.001	0	0.001
2-Hydroxy-2-phenylpropane	0.004	0	0.004
Cumene hydroperoxide	0.02	0	0.02
Water	1.05	0.005	1.040
Total	8.40	6.06	2.34

[a] Personal communication with L. B. Evans, 9 February 1976.

a demister. The gaseous stream then is passed through a refrigerated condenser, separated from the liquid, and passed through a demister before it is released to the atmosphere (Stream B). Liquid collected in the two separators is recycled (Stream C). The control efficiency is 99.6% by weight for total organic materials.

2. Activated Carbon Adsorption

Adsorption is a phenomenon in which molecules become attached to the surface of a solid. The process is highly selective, and a given adsorbent, or adsorbing agent, will adsorb only certain types of molecules. The material adhering to the adsorbent is called the adsorbate (24). Adsorption involves three steps. First, the adsorbent comes in contact with the stream containing the adsorbate, and separation due to adsorption results. Next, the unadsorbed portion of the stream is separated form the adsorbent. Finally, the adsorbent is regenerated by removing the adsorbate.

Activated carbon is the most suitable adsorbent for organic vapors(24). Carbon adsorbs 95% to 98% of all organic vapor from air at ambient temperature regardless of variations in concentration and humidity given a sufficent quantity of carbon. The adsorption of a mixture of organic vapors in air by carbon is not uniform (48), however, higher boiling point components are preferentially adsorbed.

When a contaminated gas stream is passed over an activated carbon bed, the organic vapor is adsorbed and the purified stream passes through. Initially, adsorption is rapid and complete, but as the carbon bed approaches its capacity to retain vapor, traces of vapor appear in the exit air. This is the breakpoint of the activated carbon. If gas flow is continued, additional amounts of organic material are adsorbed, but at a decreasing rate (24).

After breakthrough has occurred, the adsorbent is regenerated by heating the solids until the adsorbate has been removed. A carrier gas must be used to remove the vapors released. Low pressure saturated steam is used as the heat source for activated carbon and also acts as the carrier gas. When high boiling compounds have reduced the carbon capacity to the point where complete regeneration is necessary, super-heated steam at 350°C may be necessary to remove high boiling compounds and return the carbon to its original condition (47). The steam is condensed and sent to the process wastewater system for disposal.

The control efficiency of carbon adsorbers is greater than 90% for cumene peroxidation vent emissions, (personal communication with L. B. Evans, 9 February 1976).

3. Solvent Absorption

Absorption is a process for removing one or more soluble components from a gas mixture by dissolving them in a solvent.

Absorption equipment is designed to insure maximum contact between the gas and the liquid solvent to permit interphase diffusion between the materials. Absorption rate is affected by factors such as the solubility of gas in the particular solvent and the degree of chemical reaction; however, the most important factor is the solvent surface exposed (24).

A vent gas scrubber-cooler system used on a cumene peroxidation vent is illustrated in Figure 19. The information known about the streams is presented in Table 34 (personal communication with L. B. Evans, 9 February 1976).

In this system off gases are scrubbed in a tray tower to absorb hydrocarbons into the scrubbing liquid, which is an aqueous Na_2CO_3 solution. Some of the scrubbing liquid is sent to the oxidation section, and some is recycled through the scrubber with makeup solution. The scrubbed gas is cooled, condensate is removed and sent to the oxidation section, and the gas is released to the atmosphere.

4. Incineration

Complete combustion of the hydrocarbons present in the emissions from a cumene peroxidation phenol plant produces carbon dioxide and water. NO_x may be produced depending on the method of combustion and the temperature. SO_x production depends on the sulfur content of the auxiliary fuel, if any. The types of

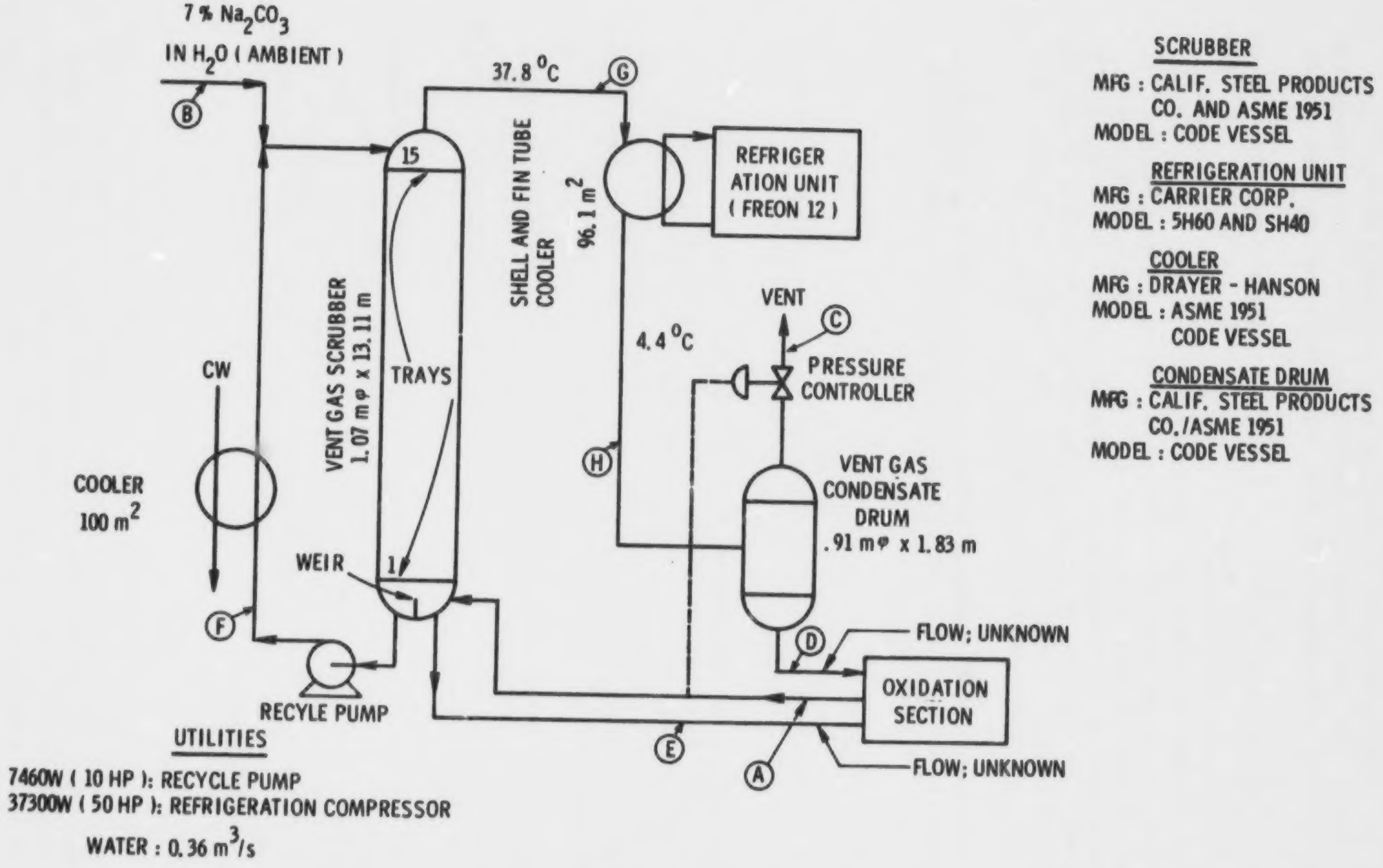
7 % Na_2CO_3
IN H_2O (AMBIENT)
B
37.8 °C
G
15
REFRIGER ATION UNIT (FREON 12)
SHELL AND FIN TUBE COOLER
96.1 m^2
VENT
C
4.4 °C
PRESSURE CONTROLLER
CW
TRAYS
VENT GAS SCRUBBER
1.07 mφ x 13.11 m
COOLER
100 m^2
H
VENT GAS CONDENSATE DRUM
.91 mφ x 1.83 m
WEIR
1
F
D
FLOW; UNKNOWN
OXIDATION SECTION
RECYLE PUMP
E
A
FLOW; UNKNOWN
UTILITIES
7460W (10 HP): RECYCLE PUMP
37300W (50 HP): REFRIGERATION COMPRESSOR
WATER : 0.36 m^3/s
SCRUBBER
MFG : CALIF. STEEL PRODUCTS CO. AND ASME 1951
MODEL : CODE VESSEL
REFRIGERATION UNIT
MFG : CARRIER CORP.
MODEL : 5H60 AND SH40
COOLER
MFG : DRAYER - HANSON
MODEL : ASME 1951 CODE VESSEL
CONDENSATE DRUM
MFG : CALIF. STEEL PRODUCTS CO./ASME 1951
MODEL : CODE VESSEL

Figure 19. Vent gas scrubber-cooler.[a]

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[a] Personal communication with L. B. Evans, 9 February 1976.

TABLE 34. STREAM INFORMATION FOR VENT GAS SCRUBBER COOLER USED ON THE CUMENE PEROXIDATION VENT[a,b]

Component	In Stream A, wt %	 Stream B,[c] wt %
O_2	7.0	
N_2	60	
Water	13	
Na_2CO_3	0	
CO_2	Trace	
Cumene	16	
Cumene hydroperoxide	Trace	
Oxidized organics	Trace	
Flow rate, m^3/s[d]	1.75	1.75
Temperature, °C	110	21.4
Pressure, kPa	551.6	3.4

[a] Personal communications with L. B. Evans, 9 February 1976.

[b] No information is available on Streams C, D, E, F, G, and H, except that Stream C contains 200 ppm of hydrocarbons.

[c] Blanks indicate no information.

[d] Basis for volume measurement as standard or actual conditions not defined.

incinerators (i.e., direct flame afterburners, catalytic afterburners, or flares), used to combust hydrocarbons at plants manufacturing acetone and phenol from cumene were not reported.

Storage Tanks, General

Six kinds of evaporation loss from storage of organic materials occur: breathing, standing storage, filling, emptying, wetting, and boiling. Vapors expelled from a tank because of thermal expansion, barometric expansion, or additional vaporization are breathing losses. Vapor loss from such areas as seals, hatches, valves, and other openings (but not due to breathing or level changes) constitute standing storage loss. Vapors expelled from a tank as it is filled constitute filling loss. Vapors expelled from the tank during emptying (due to the fact that vaporization occurs slowly, air enters to equalize pressure, vaporization stabilizes, and there is excess vapor in the tank) are emptying loss. Wetting loss is the vaporization of liquid from wetted exposed wall in a floating roof tank when the roof is lowered. Vapors expelled because of boiling are boiling loss.

Floating Roof Tanks

Floating roof tanks are of various designs but the basic concept is that the roof floats on the surface of the stored material. A seal provides intimate contact between the roof and the tank wall. These tanks reduce breathing and filling losses by reducing the space available for vapor accumulation. Wetting losses are small and not a problem (50).

Sealed Dome Roof Tanks

This type of tank can withstand relatively large pressure variations without incurring a loss. There is little or no breathing loss. Filling loss will depend on the tank design (50).

Conservation Vent for Tanks

The conservation vent is a device to inhibit evaporation loss while protecting the tank from possible damage due to underpressure or overpressure. The vent has two set points, an upper and a lower pressure. If the pressure is outside this range the vent opens to allow pressure equalization with the atmosphere (51). This reduces evaporation losses.

Vapor Recovery System on Product Loading Facilities

This control device collects the vapors produced from product loading and disposes of them by one of the control methods previously described, such as condensation, adsorption, etc. (24). Vapor recovery is a general term for emission control practices.

Fugitive Emission Control

Fugitive emissions are controlled by preventive maintenance programs, double seals on pumps, and other measures of this type to eliminate or reduce emissions from relief valves, pump seals, compressor seals, pipeline valves and flanges, and process drains.

FUTURE CONSIDERATIONS

Air Resources, Inc., and Harshaw Chemical Co., have developed a catalytic incinerator that permits lower temperature operation and lower fuel costs than thermal or flame incineration techniques for treatment of organic emissions (52). A pilot demonstration program at the Clark Oil and Refining Corp., Clark Chemical Corp., phenol plant in Blue Island, Illinois, was successful. Good catalyst activity for a variety of organic compounds and a low catalyst deactivation rate were observed (52). This method could prove feasible on a large scale, and economically attractive, if the claims are correct.

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(50) Evaporation Loss in the Petroleum Industry - Causes and Control. Bulletin 2513, American Petorleum Institute, New York, New York, February 1959. 57 pp.

(51) Use of Pressure-Vacuum Vent Valves for Atmospheric Pressure Tanks to Reduce Evaporation Loss. Bulletin 2521, American Petroleum Institute, New York, New York, September 1966. 14 pp.

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(52) Hardison, L. C., and E. J. Dowd. Air Pollution Control: Emission Control Via Fluidized Bed Oxidation. Chemical Engineering Progress, 73(8):31-35, 1977.

SECTION 6

GROWTH AND NATURE OF THE INDUSTRY

Phenol is used in the production of resins, caprolactam, bisphenol A, alkyl phenols, adipic acid, and salicylic acid (2, 53, 54). The markets for these products are expected to grow, leading to a projected 1982 phenol capacity in the United States of 2,050 x 10^3 metric tons (53, 54). Of that capacity, 92% is projected to be based on cumene.

Acetone is used in the production of methyl isobutyl ketone, methyl-acrylate esters, protective coatings, solvent derivatives, cellulose acetate, bisphenol A, pharmaceuticals, and acetylene (3, 55-57). The coproduction of acetone from the cumene peroxidation phenol process in 1982 could account for approximately 71% of the projected acetone demand. However, since acetone is a product of phenol production, strong phenol demand could cause an acetone surplus.

This section contains the information collected on available technologies to produce phenol and acetone. Emerging technologies and possible modifications to the cumene peroxidation process are discussed. Market and use trends for phenol, acetone, acetophenone, cumene hydroperoxide, and α-methylstyrene are presented. Production trends for phenol are also discussed and projected to 1980 and 1982.

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(53) Chemical Profile, Phenol. Chemical Marketing Reporter, 207(7):9, 1975.

(54) Chemical Briefs, Phenol. Chemical Purchasing, 10(4):27-32, 1974.

(55) Chemical Profile, Acetone. Chemical Marketing Reporter, 206(21):9, 1974.

(56) Acetone. Chemical Purchasing, (10(6):24-27, 1974.

(57) Chemical Briefs, Acetone. Chemical Purchasing, 10(3):32-48, 1974.

PROCESS TECHNOLOGY

Phenol

Phenol can be commercially produced from benzene, chlorobenzene, toluene, and natural sources (4, 7, 58, 59). Figure 20 displays the chemical relationships between the major synthetic phenol processes. A brief description of each major process and of other possible processes is given below.

Chlorobenzene Process--

Only one plant, comprising approximately 4% of the 1976 total synthetic phenol capacity in the continental United States, uses this process. The feedstock may be either benzene or chlorobenzene. Benzene and chlorine are reacted at 80°C to produce chlorobenzene, HCl, and about 5% polychlorobenzenes (7, 54, 56, 57). The chlorobenzene is hydrolyzed at 400°C to 500°C and 27.6 MPa to 34.5 MPa (4,000 psi to 5,000 psi) with a catalyst to produce a stream of sodium phenate sodium chloride, and unchanged reactants (4, 7, 20, 22). Sodium phenate is treated with HCl to produce phenol and sodium chloride. The NaCl is often electrolyzed to form NaOH and chlorine. The byproducts, 2-biphenylol, 4-biphenylol, and phenyl ether, must also be recovered to make the process economical (4, 7, 21, 23, 58-64). The overall phenol

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(58) Hahn, A. V., R. Williams, and H. Zabel. The Petrochemical Industry. McGraw-Hill Book Co., New York, New York, 1970. 620 pp.

(59) Witt, P. A., Jr., and M. C. Forbes. By-Product Recovery Via Solvent Extraction. Chemical Engineering Progress, 67(10: 90-94, 1971.

(60) U.S. Petrochemicals: Technologies, Markets, and Economics; A. M. Brownstein, ed. The Petroleum Publishing Company, Tulsa, Oklahoma, 1972. 351 pp.

(61) Sittig, M. Pollution Control in the Organic Chemicals Industry. Noyes Data Corporation, Park Ridge, New Jersey, 1974. 305 pp.

(62) Background Information for Establishment of Standards of Air Pollution Control in the Petrochemical Indsutry: Benzene and Xylene Products and Carbon Black. Office of Air Programs, U.S. Environmental Protection Agency, 13 August 1971. pp. 1 through 7 and D-1 through D-20.

(63) Banciu, A. S. Phenol Manufacture. Chemical and Process Engineering, 48(1):31-35, 1967.

(64) Hay, J. M., D. W. Stirling, and C. W. Weaver. How Synthetic Phenol Processes Compare. Oil and Gas Journal, 64(1);83-88, 1966.

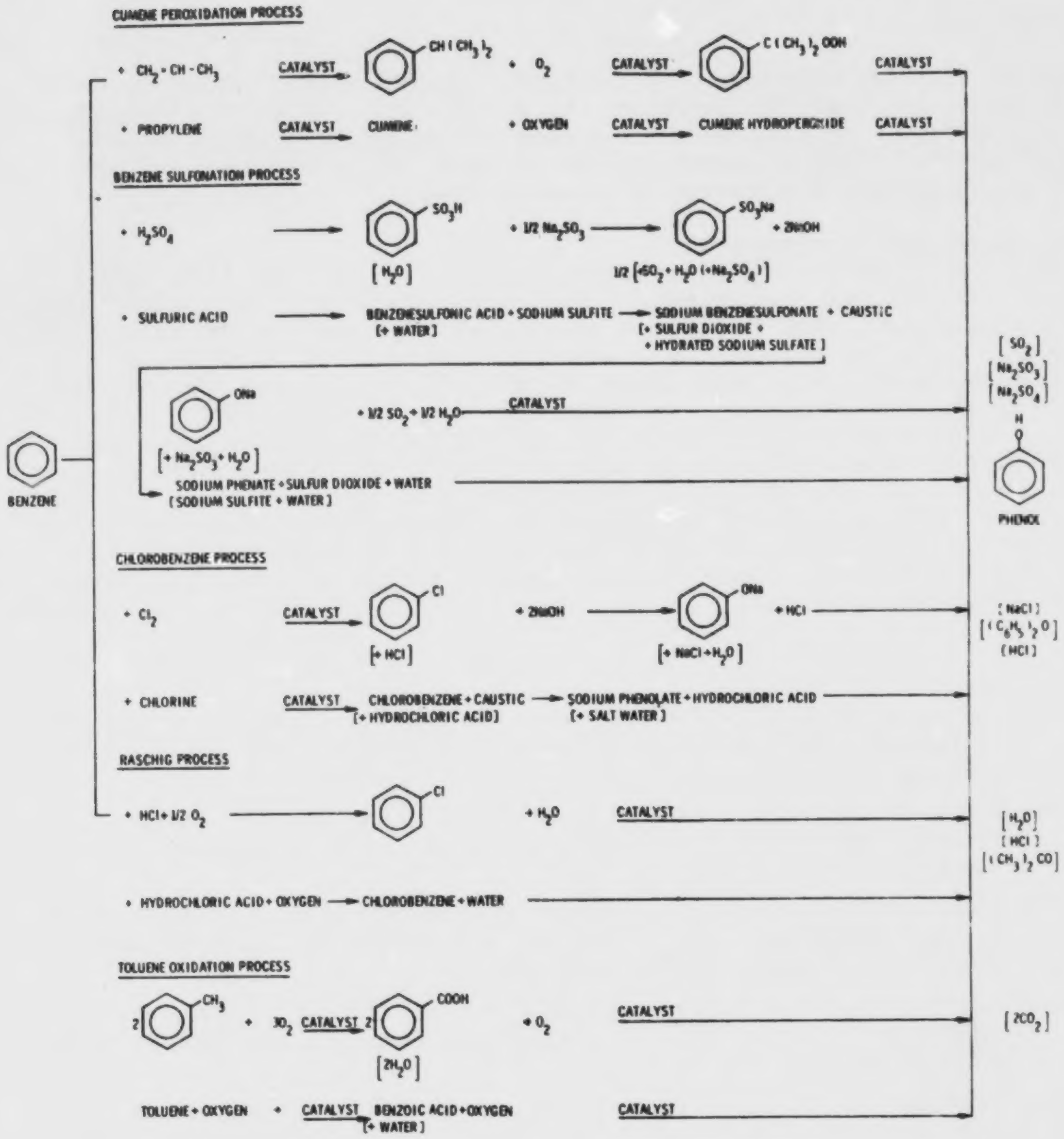
CUMENE PEROXIDATION PROCESS
+ CH2 = CH - CH3
CATALYST
CH(CH3)2
+ O2
CATALYST
C(CH3)2OOH
CATALYST
+ PROPYLENE
CATALYST
CUMENE
+ OXYGEN
CATALYST
CUMENE HYDROPEROXIDE
CATALYST
BENZENE SULFONATION PROCESS
+ H2SO4
SO3H
[H2O]
+ 1/2 Na2SO3
SO3Na
+ 2NaOH
1/2 [+SO2 + H2O (+Na2SO4)]
+ SULFURIC ACID
BENZENESULFONIC ACID + SODIUM SULFITE
[+ WATER]
SODIUM BENZENESULFONATE + CAUSTIC
[+ SULFUR DIOXIDE +
+ HYDRATED SODIUM SULFATE]
ONa
+ 1/2 SO2 + 1/2 H2O
CATALYST
[+ Na2SO3 + H2O]
SODIUM PHENATE + SULFUR DIOXIDE + WATER
[SODIUM SULFITE + WATER]
BENZENE
[SO2]
[Na2SO3]
[Na2SO4]
H
O
PHENOL
CHLOROBENZENE PROCESS
+ Cl2
CATALYST
Cl
[+ HCl]
+ 2NaOH
ONa
[+ NaCl + H2O]
+ HCl
[NaCl]
[(C6H5)2O]
[HCl]
+ CHLORINE
CATALYST
CHLOROBENZENE + CAUSTIC
[+ HYDROCHLORIC ACID]
SODIUM PHENOLATE + HYDROCHLORIC ACID
[+ SALT WATER]
RASCHIG PROCESS
+ HCl + 1/2 O2
Cl
+ H2O
CATALYST
[H2O]
[HCl]
[(CH3)2CO]
+ HYDROCHLORIC ACID + OXYGEN
CHLOROBENZENE + WATER
TOLUENE OXIDATION PROCESS
2
CH3
+ 3O2
CATALYST
2
COOH
[2H2O]
+ O2
CATALYST
[2CO2]
TOLUENE + OXYGEN
+
CATALYST
BENZOIC ACID + OXYGEN
[+ WATER]
CATALYST

Figure 20. Chemical relationship between major synthetic phenol processes.[a]

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[a] [] indicate byproducts produced from reactions.

yield is 81% based on the weight of benzene input to the process (65).

Sulfonation Process--

One plant, which has 5.5% of the 1976 total synthetic phenol capacity of the continental United States, uses this process. Vaporized benzene is contacted with concentrated sulfuric acid at approximately 150°C to produce benzenesulfonic acid and water (4, 7, 21, 23, 58-64). The benzenesulfonic acid is neutralized with sodium sulfite which produces sodium benzenesulfonate, sodium sulfate, and sulfur dioxide. Caustic fusion of the sodium benzenesulfonate at 300°C to 380°C for five to six hours produces a sodium phenate-sodium hydroxide-sodium sulfate solution. This solution is then acidified with sulfur dioxide and sulfuric acid to form phenol and sodium sulfite. The yield is approximately 75% phenol, based on the weight of benzene charged to the reactor (65). A variant of the process is to caustic-fuse the benzene-sulfonic acid, and then treat with dilute sulfuric acid to produce phenol, with sodium sulfate as a byproduct.

Raschig and Raschig-Hooker Process--

At this time there are no plants in the United States using this process. All plants that were using this process were phased out between 1972 and the present (4, 7, 21, 23, 58-64). The Raschig process was originally developed in the 1930's and later modified to the Raschig-Hooker Process. Benzene is chlorinated in the vapor phase, at 220°C to 300°C and approximately atmospheric pressure, with gaseous hydrochloric acid over a catalyst. The chlorobenzene produced contains approximately 6% polychlorinated benzenes. The chlorobenzene is hydrolyzed over a catalyst at 400°C to 500°C to produce phenol and hydrochloric acid. Benzene is converted to chlorobenzene at a rate of 10% per pass over the catalyst. The conversion of chlorobenzene to phenol is 10%, with the reaction proceeding at a selectivity of less than 10% for phenol. The low reaction rates and selectivities necessitate numerous separation and recycle steps. The overall yield is 80% phenol, based on the weight of benzene consumed (65).

Cumene Peroxidation Process--

The cumene to phenol process is described in detail in Section 3. The long version of the process includes the reaction of benzene and propylene in the presence of a catalyst to form cumene. The yield is 81% based on the weight of benzene reacted (65).

Toluene Oxidation Process--

This process accounts for 1.6% of the 1976 total synthetic phenol capacity of the continental United States, and is used in only one plant (4, 7, 21, 58, 60). Toluene is oxidized to benzoic acid by passing air through liquid toluene in the presence of a catalyst, at 125°C or above and two atmospheres pressure or above. A distilled benzoic acid stream is reacted with air and steam, in the presence of a catalyst, at 230°C and 138 kPa (20 psi to 25 psi) to form phenol. The yield is 78% phenol, based on the weight of toluene (65).

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(65) Blackford, J. L. Chemical Conversion Factors and Yields. Chemical Information Services, Menlo Park, California, 1977. pp. 3, 76.

Benzene Oxidation Process (20)--

Schenectady Chemical Co., in Rotterdam Junction, New York, once operated a plant using this process. Little information about the process was found, except that its yields were poor compared to other processes. No U.S. producers currently use this process.

Cyclohexane Oxidation Process (7)--

Cyclohexane is oxidized to cyclohexanone and cyclohexanol, which are dehydrogenated to produce phenol. This process has been used commercially in other countries, but is not currently being used in the United States.

Natural Sources (2, 31, 66-72)--

Five firms in the continental United States produce phenol from natural sources. Natural phenol is recovered from coke ovens,

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(66) Preliminary Report on U.S. Production of Selected Synthetic Organic Chemicals; November, December, and Cumulative Totals, 1977. S.O.C. Series C/P-77-12, United States International Trade Commission, Washington, D.C., 15 February 1978. 3 pp.

(67) Synthetic Organic Chemicals, United States Production and Sales, 1975. USITC Publication 804, United States International Trade Commission, Washington, D.C., 1977. pp. 39, 40, 214.

(68) Synthetic Organic Chemicals, United States Production and Sales, 1974. USITC Publication 776, United States International Trade Commission, Washington, D.C., 1976. pp. 22, 39, 42.

(69) Synthetic Organic Chemicals, United States Production and Sales, 1973. USITC Publication 728, United States International Trade Commission, Washington, D.C., 1975. p. 23.

(70) Synthetic Organic Chemicals, United States Production and Sales, 1972. TC Publication 681, United States Tariff Commission, Washington, D.C., 1974. p. 22.

(71) Synthetic Organic Chemicals, United States Production and Sales, 1971. TC Publication 614, United States Tariff Commission, Washington, D.C., 1973. p. 22.

(72) Synthetic Organic Chemicals, United States Production and Sales, 1970. TC Publication 479, United States Tariff Commission, Washington, D.C., 1972. p. 24.

coal tars, and petroleum operations. The importance of natural phenol is declining (see Table 35). Natural phenol accounted for 2.7% of the total U.S. production of phenol in 1970 and 1.3% in 1976.

TABLE 35. U.S. PRODUCTION OF PHENOL (2, 31, 66-72)
(10^3 metric tons)

Year	Natural	Cumene based	Other synthetic	Total synthetic	Total
1976	13.1	-[a]	-[a]	990.4[b]	1,003.5[b]
1975	-[a]	703.0[b]	89.2	792.2[b]	-[a]
1974	13.8	947.0[b]	95.4	1,042.4[b]	1,056.2[b]
1973	15.7	914.6[b]	102.0	1,016.6[b]	1,032.3[b]
1972	20.1	821.4[b]	109.3	930.7[b]	950.8[b]
1971	18.4	629.8	161.1	790.9	809.3
1970	21.4	529.6	245.5	775.1	796.5

[a] Not available.

[b] Includes Puerto Rico's contribution.

Acetone

Acetone may be produced in a variety of ways. A brief description of each technology is given below.

Cumene Peroxidation Process (5)--

Acetone is produced as a byproduct of this process, which is described in detail in Section 3.

Catalytic Dehydrogenation of Isopropyl Alcohol (4, 5)--

Acetone is produced from vapor phase dehydrogenation of isopropyl alcohol at 325°C to 500°C and 275 kPa to 350 kPa (40 psi to 50 psi) over a catalyst. The yield of acetone is 95% by weight based on isopropyl alcohol.

Catalytic Oxidation-Dehydrogenation Process (4, 5)--

The above process can be modified to produce acetone from a mixture of isopropyl alcohol and air at 400°C to 500°C over a catalyst. The yield is 85% to 90% acetone by weight based on isopropyl alcohol.

Fermentation Process (4, 5)--

Acetone is one of several substances produced by distillation of the mixture resulting from the fermentation of diluted sterile molasses by a bacteria culture. The overhead product is a mixture of normal butyl alcohol, acetone, and ethyl alcohol. The bottoms contain proteins and vitamins. The solvent yield is 28% to 33% by weight of sugar charged.

Wacker Process (7)--
The Wacker process produces acetone by oxidation of propylene over a palladium catalyst.

Propylene Oxidation Process (7)--
The oxidation of propylene to propylene oxide produces crude acetone as a byproduct.

Glycerol Process (5)--
Acrolein is produced by vapor phase oxidation of propylene over a catalyst. Isopropyl sulfate is then produced by abdorbing the propylene in sulfuric acid, and the isopropyl sulfate is hydrolyzed to isopropyl alcohol. Acrolein and isopropyl alcohol are reacted to form acetone and allyl alcohol. Liquid isopropyl alcohol is sparged with oxygen to form acetone and hydrogen peroxide. The hydrogen peroxide is used to convert allyl alcohol to glycerol, and acetone is obtained as a byproduct.

Propane-butane Oxidation (7)--
Acetone is one of a number of oxygenated compounds which are formed during the oxidation of propane-butane mixture.

Wood Distilling Industry Process (5)--
The dry distillation of calcium acetate produces acetone. Calcium acetate is obtained by neutralizing pyroligneous acid with lime and evaporating.

Steam Hydrolysis (58)--
In Romania, acetone has been produced by the steam hydrolysis of acetylene over a catalyst.

Hydrogen Peroxide Process (4)--
Acetone is a byproduct of the manufacture of hydrogen peroxide by isopropyl alcohol oxidation.

Hydroquinone Production (4)--
Acetone is a coproduct from the manufacture of hydroquinone from *p*-diisopropyl benzene.

Butene Dehydrogenation (4)--
Acetone can be a coproduct from the dehydrogenation of butene to methyl ethyl ketone (MEK).

Important Byproducts

Acetophenone--
This compound can be produced as a byproduct from the cumene peroxidation product of phenol, oxidation of ethylbenzene, or the Friedel-Crafts reaction of benzene, aluminum chloride, and acetic anhydride (5). The Friedel-Crafts reaction was the principal source before 1949, but is not in use today.

α-Methylstyrene--
This compound can be produced as a byproduct of the cumene peroxidation production of phenol or by the dehydrogenation of cumene (11).

EMERGING TECHNOLOGY

The trend in phenol production has been a shift to manufacture from cumene (see Table 36), which is economically favored (7). Research is currently being done on the process to find improvements. Some of the ideas under consideration are: 1) the use of oxygen instead of air in order to reduce reactor volume and atmospheric emissions, 2) hydrocarbon recovery systems to enable best usage of feedstocks, and 3) pump seal improvements (4, 7, 12, 13).

The future of acetone processing is intimately related to the growth of the cumene process for phenol. As phenol growth continues, more acetone will be available at low coproduct prices (4, 12, 13). Cumene peroxidation coproduct acetone has accounted for an increasing share of the acetone market (3, 56, 57). In 1970, 405 x 10^3 metric tons of acetone were produced from all other processes, and 328 x 10^3 metric tons of acetone were produced from the cumene peroxidation process (70). The cumene peroxidation total accounted for 45% of the acetone produced in 1968. In 1975, 312 x 10^3 metric tons of acetone were produced from all other processes and 432 x 10^3 metric tons of acetone were produced from the cumene peroxidation process (4, 56, 57, 61). The cumene peroxidation process accounted for 58.1% of the acetone produced in 1975.

INDUSTRY PRODUCTION TRENDS

Phenol

Phenol is an intermediate synthetic organic chemical with many uses and markets, which are summarized in Figure 21 (73).

Table 37 shows the relative amount of phenol consumed in each major market area during 1974, 1975, and 1977 (2, 32, 53, 54).

The major use for phenol is phenolic resins which are used as moldings in the automotive, appliance, and electrical industries, and as adhesives in the bonding and laminating of plywood and

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(73) Chemical Origins and Markets, Flow Charts and Tables, Fifth Edition. Chemical Information Services, Stanford Research Institute, Menlo Park, California, 1977. 118 pp.

TABLE 36. PHENOL CAPACITY AND PRODUCTION

Year	Capacity, 10^3 metric tons/yr		Percent of cumene based capacity	Production, 10^3 metric tons/yr		Percent of cumene based production
	Total	Cumene based		Total	Cumene based	
1977	1,468	1,358	93	1,083[a,b,c]	-[d]	-[d]
1976	1,193	1,054	88	1,004[a,b,c]	-[d]	-[d]
1975	1,132	1,020	90	792	703	89
1974	1,175	1,002	85	1,056	947	90
1973	-[d]	-[d]	-[d]	1,032[a,c]	915	89
1972	1,145	955	83	951[a,c]	821	86
1971	1,347	1,048	78	809[c]	630	78
1970	959	660	69	797[c]	530	67
1969	875	-[d]	-[d]	768[c]	434	57
1968	728	404	55	686[c]	381	56
1967	680	-[d]	-[d]	615[c]	327	53
1966	605	249	41	611[c]	278	45
1965	583	249	43	557[c]	254	46
1964	508	-[d]	-[d]	505[c]	201	40

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[a] Includes Puerto Rico's contribution.

[b] Preliminary.

[c] Includes natural sources.

[d] Not available.

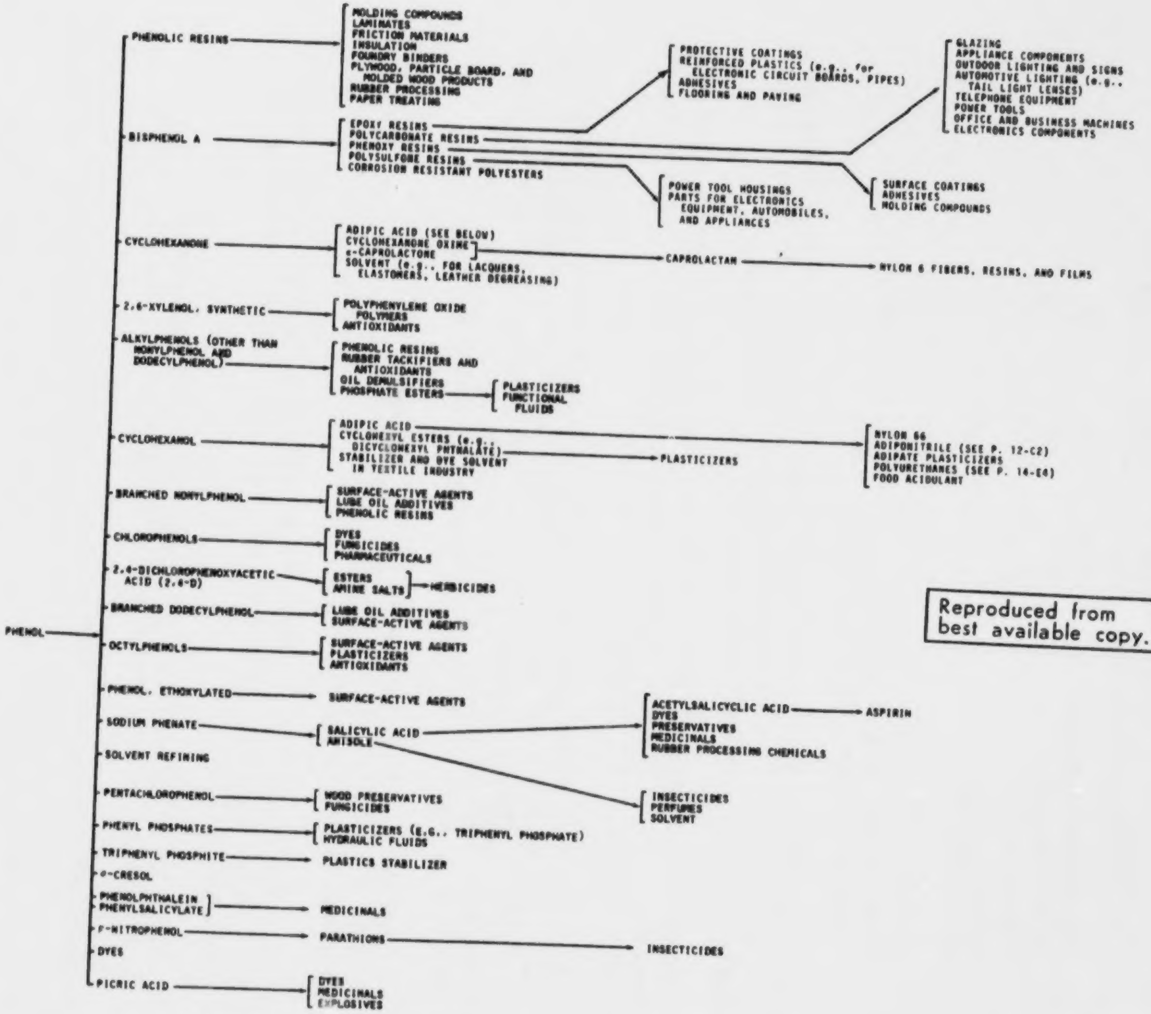
PHENOL
PHENOLIC RESINS
MOLDING COMPOUNDS
LAMINATES
FRICTION MATERIALS
INSULATION
FOUNDRY BINDERS
PLYWOOD, PARTICLE BOARD, AND MOLDED WOOD PRODUCTS
RUBBER PROCESSING
PAPER TREATING
BISPHENOL A
EPOXY RESINS
POLYCARBONATE RESINS
PHENOXY RESINS
POLYSULFONE RESINS
CORROSION RESISTANT POLYESTERS
PROTECTIVE COATINGS
REINFORCED PLASTICS (e.g., for ELECTRONIC CIRCUIT BOARDS, PIPES)
ADHESIVES
FLOORING AND PAVING
GLAZING
APPLIANCE COMPONENTS
OUTDOOR LIGHTING AND SIGNS
AUTOMOTIVE LIGHTING (e.g., TAIL LIGHT LENSES)
TELEPHONE EQUIPMENT
POWER TOOLS
OFFICE AND BUSINESS MACHINES
ELECTRONICS COMPONENTS
POWER TOOL HOUSINGS
PARTS FOR ELECTRONICS EQUIPMENT, AUTOMOBILES, AND APPLIANCES
SURFACE COATINGS
ADHESIVES
MOLDING COMPOUNDS
CYCLOHEXANONE
ADIPIC ACID (SEE BELOW)
CYCLOHEXANONE OXIME
ε-CAPROLACTONE
SOLVENT (e.g., FOR LACQUERS, ELASTOMERS, LEATHER DEGREASING)
CAPROLACTAM
NYLON 6 FIBERS, RESINS, AND FILMS
2,6-XYLENOL, SYNTHETIC
POLYPHENYLENE OXIDE POLYMERS
ANTIOXIDANTS
ALKYLPHENOLS (OTHER THAN NONYLPHENOL AND DODECYLPHENOL)
PHENOLIC RESINS
RUBBER TACKIFIERS AND ANTIOXIDANTS
OIL DEMULSIFIERS
PHOSPHATE ESTERS
PLASTICIZERS
FUNCTIONAL FLUIDS
CYCLOHEXANOL
ADIPIC ACID
CYCLOHEXYL ESTERS (e.g., DICYCLOHEXYL PHTHALATE)
STABILIZER AND DYE SOLVENT IN TEXTILE INDUSTRY
PLASTICIZERS
NYLON 66
ADIPONITRILE (SEE P. 12-C2)
ADIPATE PLASTICIZERS
POLYURETHANES (SEE P. 14-E4)
FOOD ACIDULANT
BRANCHED NONYLPHENOL
SURFACE-ACTIVE AGENTS
LUBE OIL ADDITIVES
PHENOLIC RESINS
CHLOROPHENOLS
DYES
FUNGICIDES
PHARMACEUTICALS
2,4-DICHLOROPHENOXYACETIC ACID (2,4-D)
ESTERS
AMINE SALTS
HERBICIDES
BRANCHED DODECYLPHENOL
LUBE OIL ADDITIVES
SURFACE-ACTIVE AGENTS
OCTYLPHENOLS
SURFACE-ACTIVE AGENTS
PLASTICIZERS
ANTIOXIDANTS
PHENOL, ETHOXYLATED
SURFACE-ACTIVE AGENTS
SODIUM PHENATE
SALICYLIC ACID
ANISOLE
ACETYLSALICYCLIC ACID
ASPIRIN
DYES
PRESERVATIVES
MEDICINALS
RUBBER PROCESSING CHEMICALS
INSECTICIDES
PERFUMES
SOLVENT
SOLVENT REFINING
PENTACHLOROPHENOL
WOOD PRESERVATIVES
FUNGICIDES
PHENYL PHOSPHATES
PLASTICIZERS (E.G., TRIPHENYL PHOSPHATE)
HYDRAULIC FLUIDS
TRIPHENYL PHOSPHITE
PLASTICS STABILIZER
o-CRESOL
PHENOLPHTHALEIN
PHENYLSALICYLATE
MEDICINALS
P-NITROPHENOL
PARATHIONS
INSECTICIDES
DYES
PICRIC ACID
DYES
MEDICINALS
EXPLOSIVES

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Figure 21. Phenol uses and markets (73).

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TABLE 37. PHENOL CONSUMPTION BY MAJOR MARKET (2, 32, 53, 54)

Uses	Percent		
	1977	1975	1974
Phenolic resins	40 to 50	46	50
Caprolactum	15	16	20
Bisphenol A	15	14	10
Adipic acid	3	3	3
All other[a]	17 to 27	21	17

[a] Includes alkyl phenols, salicylic acid, exports, and miscellaneous uses.

fiber board. Further growth in this area is tied to the housing, automotive, and highway construction industries (2, 32, 53, 54). These industries are now showing increasing strength.

Caprolactum is the monomer for nylon 6 fibers, polyamide film and molding resins. This phenol market is forecast to increase at approximately 6% to 7.5% per year (32, 72).

Bisphenol A, another major phenol-based product is a principal raw material for epoxy and polycarbonate resin manufacture (2, 4, 32, 53, 54, 72). These resins are used in protective coatings, molded products, and road and runway surfaces (2, 32, 53, 54, 72). Bisphenol A is the fastest growing market for phenol.

The use of phenol in the production of adipic acid (used in nylon manufacturing) is expected to decline because competitive fibers can be produced more economically (2, 4, 7, 53, 54, 73).

Alkyl phenols are used in lubricating oil additives, oil-compatible resins, nonionic surface active agents, rubber chemicals, and antioxidants (72).

Salicylic acid is used in the manufacture of pharmaceuticals, especially aspirin (acetylsalicylic acid) (2, 4, 7, 54, 72).

Miscellaneous market areas for phenol include perfume ingredients, photographic developers, dyes, herbicides, insecticides, solvents, and preservatives (2, 4, 7, 53, 54, 73).

Acetone

Acetone has a wide variety of uses because of its solvent properties. The primary outlet until 1950 was as a solvent.

Table 38 presents the usage (in percent) of acetone in its major market areas in 1977 and 1974 (3, 55, 57).

TABLE 38. ACETONE CONSUMPTION BY MAJOR MARKET (3, 55, 57)

Uses	Percent 1977	Percent 1974
Methyl methacrylate and esters	35	31
Methyl isobutyl ketone	13	14
Coatings solvent	10	10
Bisphenol A	7	5
Cellulose acetate	5	5
Pharmaceutical	5.5	5.5
Exports	3.4	6
All other	21.1	23.5

These, and other markets for acetone are shown in Figure 22 (73). Methyl isobutyl ketone is a potentially troubled market because of air pollution controls that may reduce usage by up to 75% (55-57).

Byproducts of the Manufacture of Acetone and Phenol from Cumene

Figure 23 depicts the uses and markets for acetophenone, cumene hydroperoxide, mesityl oxide, and α-methylstyrene (73).

OUTLOOK

Projection of the historical information on phenol production and demand in Table 36 led to the results in Figures 24 and 25. Projections for 1980 and 1982 are given in Table 39 (2, 21, 22, 31, 56-64, 74-79).

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(74) Synthetic Organic Chemicals, United States Production and Sales, 1969. TC Publication 412, United States Tariff Commission, Washington, D.C., 1971. p. 25.

(75) Synthetic Organic Chemicals, United States Production and Sales, 1968. TC Publication 327, United States Tariff Commission, Washington, D.C., 1970. p. 25.

(76) Synthetic Organic Chemicals, United States Production and Sales, 1967. TC Publication 295, United States Tariff Commission, Washington, D.C., 1969. p. 13.

(77) Synthetic Organic Cehmicals, United States Production and Sales, 1966. TC Publication 248, United States Tariff Commission, Washington, D.C., 1968. p. 14.

(78) Synthetic Organic Chemicals, United States Production and Sales, 1965. TC Publication 206, United States Tariff Commission, Washington, D.C., 1967. p. 14.

(continued)

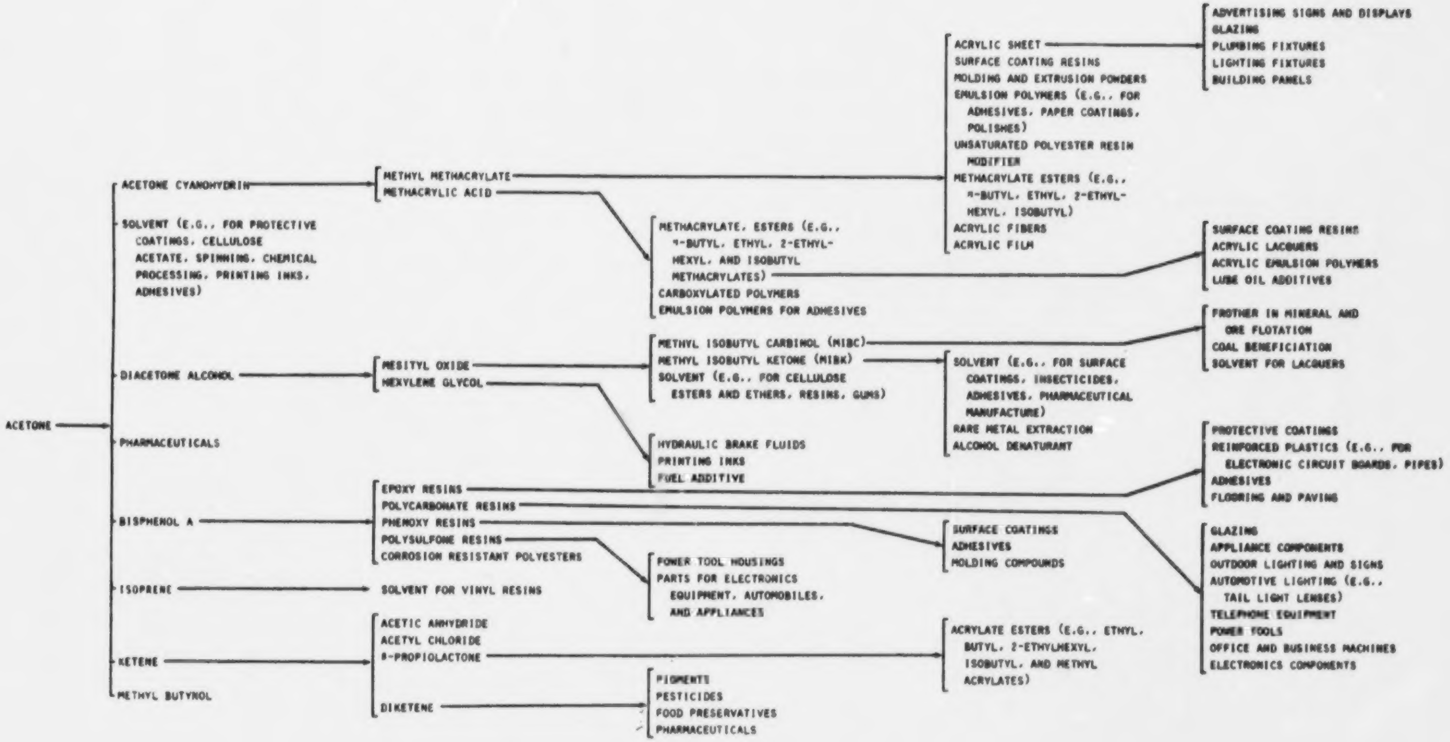
ACETONE
ACETONE CYANOHYDRIN
SOLVENT (E.G., FOR PROTECTIVE COATINGS, CELLULOSE ACETATE, SPINNING, CHEMICAL PROCESSING, PRINTING INKS, ADHESIVES)
DIACETONE ALCOHOL
PHARMACEUTICALS
BISPHENOL A
ISOPRENE
KETENE
METHYL BUTYNOL
METHYL METHACRYLATE
METHACRYLIC ACID
MESITYL OXIDE
HEXYLENE GLYCOL
EPOXY RESINS
POLYCARBONATE RESINS
PHENOXY RESINS
POLYSULFONE RESINS
CORROSION RESISTANT POLYESTERS
SOLVENT FOR VINYL RESINS
ACETIC ANHYDRIDE
ACETYL CHLORIDE
β-PROPIOLACTONE
DIKETENE
METHACRYLATE, ESTERS (E.G., n-BUTYL, ETHYL, 2-ETHYLHEXYL, AND ISOBUTYL METHACRYLATES)
CARBOXYLATED POLYMERS
EMULSION POLYMERS FOR ADHESIVES
METHYL ISOBUTYL CARBINOL (MIBC)
METHYL ISOBUTYL KETONE (MIBK)
SOLVENT (E.G., FOR CELLULOSE ESTERS AND ETHERS, RESINS, GUMS)
HYDRAULIC BRAKE FLUIDS
PRINTING INKS
FUEL ADDITIVE
POWER TOOL HOUSINGS
PARTS FOR ELECTRONICS EQUIPMENT, AUTOMOBILES, AND APPLIANCES
PIGMENTS
PESTICIDES
FOOD PRESERVATIVES
PHARMACEUTICALS
ACRYLIC SHEET
SURFACE COATING RESINS
MOLDING AND EXTRUSION POWDERS
EMULSION POLYMERS (E.G., FOR ADHESIVES, PAPER COATINGS, POLISHES)
UNSATURATED POLYESTER RESIN MODIFIER
METHACRYLATE ESTERS (E.G., n-BUTYL, ETHYL, 2-ETHYLHEXYL, ISOBUTYL)
ACRYLIC FIBERS
ACRYLIC FILM
SOLVENT (E.G., FOR SURFACE COATINGS, INSECTICIDES, ADHESIVES, PHARMACEUTICAL MANUFACTURE)
RARE METAL EXTRACTION
ALCOHOL DENATURANT
SURFACE COATINGS
ADHESIVES
MOLDING COMPOUNDS
ACRYLATE ESTERS (E.G., ETHYL, BUTYL, 2-ETHYLHEXYL, ISOBUTYL, AND METHYL ACRYLATES)
ADVERTISING SIGNS AND DISPLAYS
GLAZING
PLUMBING FIXTURES
LIGHTING FIXTURES
BUILDING PANELS
SURFACE COATING RESINS
ACRYLIC LACQUERS
ACRYLIC EMULSION POLYMERS
LUBE OIL ADDITIVES
FROTHER IN MINERAL AND ORE FLOTATION
COAL BENEFICIATION
SOLVENT FOR LACQUERS
PROTECTIVE COATINGS
REINFORCED PLASTICS (E.G., FOR ELECTRONIC CIRCUIT BOARDS, PIPES)
ADHESIVES
FLOORING AND PAVING
GLAZING
APPLIANCE COMPONENTS
OUTDOOR LIGHTING AND SIGNS
AUTOMOTIVE LIGHTING (E.G., TAIL LIGHT LENSES)
TELEPHONE EQUIPMENT
POWER TOOLS
OFFICE AND BUSINESS MACHINES
ELECTRONICS COMPONENTS

Figure 22. Uses and markets for acetone and derivatives (73).

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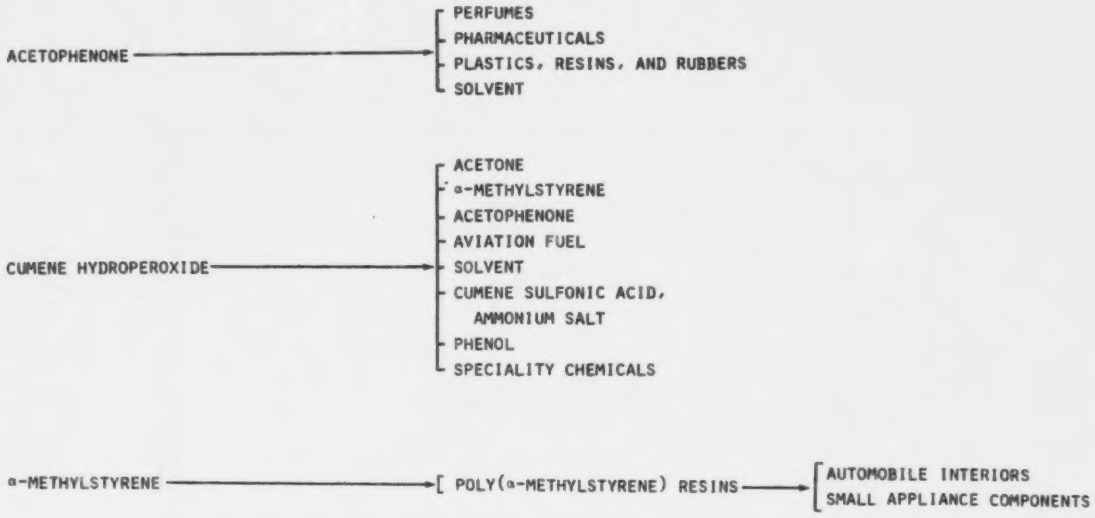
ACETOPHENONE
PERFUMES
PHARMACEUTICALS
PLASTICS, RESINS, AND RUBBERS
SOLVENT
CUMENE HYDROPEROXIDE
ACETONE
α-METHYLSTYRENE
ACETOPHENONE
AVIATION FUEL
SOLVENT
CUMENE SULFONIC ACID, AMMONIUM SALT
PHENOL
SPECIALITY CHEMICALS
α-METHYLSTYRENE
POLY(α-METHYLSTYRENE) RESINS
AUTOMOBILE INTERIORS
SMALL APPLIANCE COMPONENTS

Figure 23. Markets and uses for acetophenone, cumene hydroperoxide, and α-methylstyrene (73).

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TABLE 39. PROJECTED PRODUCTION AND CAPACITY FOR PHENOL, 1980 AND 1982 (2, 21, 22, 31, 56-64, 74-79)

Production/capacity	Projections 1980	Projections 1982
Production:		
Phenol, 10^3 metric tons	1,225	1,350
Cumene based phenol, 10^3 metric tons	1,100	1,240
Percent of cumene based production	90	92
Capacity:		
Phenol, 10^3 metric tons	1,850	2,050
Cumene based phenol, 10^3 metric tons	1,675	1,890
Percent of cumene based capacity	91	92

(continued)

(79) Synthetic Organic Chemicals, United States Production and Sales, 1964. TC Publication 167, United States Tariff Commission, Washington, D.C., 1965. p. 13.

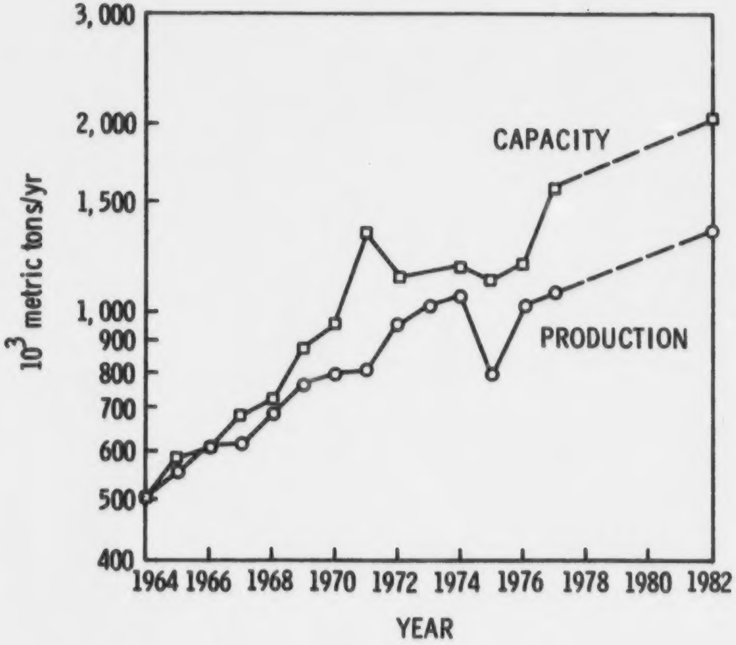

Figure 24. Capacity and production trends for phenol projected to 1978 (2, 21, 22, 31, 56-64, 56-64, 74-79).

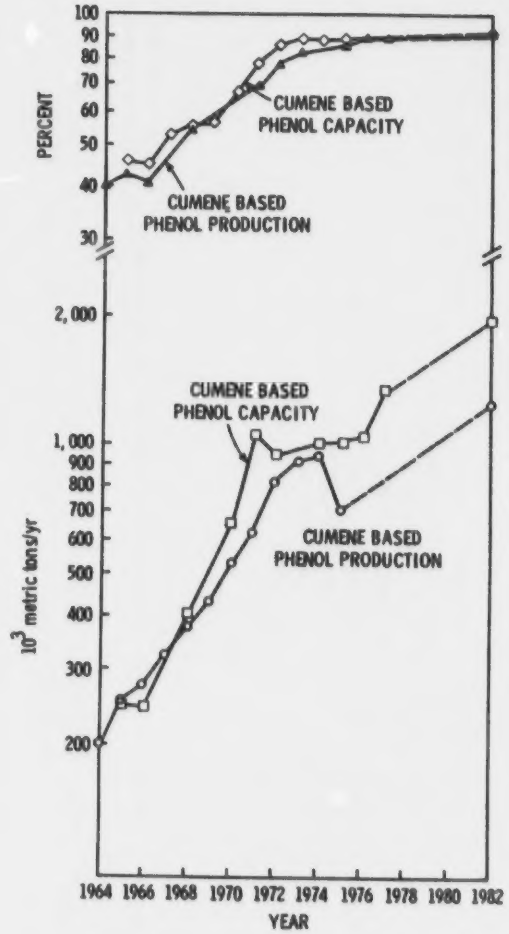

Figure 25. Historical and projected trends in cumene-based phenol production and capacity (2, 21, 22, 31, 56-64, 74-79).

Thus, phenol demand and capacity is expected to increase at an annual rate of 5% (2). However, the announced expansions and new facilities, which are listed in Table 40 would bring the phenol capacity to 2,220 x 10^3 metric tons by 1982 (2, 27, 32, 33 and personal communication with C. Paris, 4 April 1978). This increase in capacity would mean decreased capacity utilization if the growth rate in demand for phenol remains as projected.

TABLE 40. ANTICIPATED EXPANSION AND NEW FACILITIES IN THE PHENOL INDUSTRY (2, 27, 32, 33)

Company and location (process)	Added phenol capacity 10^3 metric tons/yr	Scheduled completion date
Expansions:		
Kalama Chemical Company Kalama, WA (toluene oxidation)	45	Postponed.
Georgia-Pacific Corporation Plaguemine, LA (Hercules cumene peroxidation process)	64	Planned.
Union Carbide Corporation Bound Brook, NJ (Allied cumene peroxidation process)	23	Planned.
U.S.S. Corporation U.S.S. Chemicals Company Haverhill, OH (Hercules cumene peroxidation process)	88	Early 1979.
New facilities:		
General Electric Mount Vernon, IN (Unknown)	181	1980.
Gulf Oil Chemicals Gulf Coast location (Unknown)	227	Late 1981.

The projected production of 1,240 x 10^3 metric tons of phenol from cumene in 1982 would yield approximately 760 x 10^3 metric tons of acetone coproduct. The projected acetone demand, using a predicted growth rate of 4%, is 1,070 x 10^3 metric tons (3). Therefore, about 71% of the acetone demand will be supplied by the manufacture of acetone and phenol from cumene. However, if the plants were to operate at full utilization, approximately 1,250 x 10^3 metric tons of acetone coproduct would be produced. Therefore, phenol demand could lead to an oversupply of acetone.

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77. Synthetic Organic Chemicals, United States Production and Sales, 1966. TC Publication 248, United States Tariff Commission, Washington, D.C., 1968. p. 14.

78. Synthetic Organic Chemicals, United States Production and Sales, 1965. TC Publication 206, United States Tariff Commission, Washington, D.C., 1967. p. 14.

79. Synthetic Organic Chemicals, United States Production and Sales, 1964. TC Publication 167, United States Tariff Commission, Washington, D.C., 1965. p. 13.

80. Evaporation Loss from Floating Roof Tanks. Bulletin 2517, American Petroleum Institute, New York, New York, February 1962. 13 pp.

81. Evaporation Loss from Fixed Roof Tanks. Bulletin 2518, American Petroleum Institute, New York, New York, June 1962. 38 pp.

82. Use of Variable Vapor Space Systems to Reduce Evaporation Loss. Bulletin 2520, American Petroleum Institute, New York, New York, September 1964. 14 pp.

83. Petrochemical Loss from Storage Tanks. Bulletin 2523, American Petroleum Institute, New York, New York, November 1969. 14 pp.

84. Hamersma, J. W., S. L. Reynolds, and R. F. Maddalene. IERL-RTP Procedures Manual: Level I Environmental Assessment. EPA-600/2-76-160a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1976. 147 pp.

85. Methods of Air Sampling and Analysis. American Public Health Association, Washington, D.C., 1972. pp. 190-198.

86. Method 3 - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight. Federal Register, 41(111): 23069-23070, 1976.

87. Bernas, B. A New Method for Decomposition and Comprehensive Analysis of Silicates by Atomic Absorption Spectrometry. Analytical Chemistry, 40(11):1682-1686, 1968.

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89. Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

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91. Tadmor, J., and Y. Gur. Analytical Expressions for the Vertical and Lateral Dispersion Coefficients in Atmospheric Diffusion. Atmospheric Environment, 3(6):688-689, 1969.

92. Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

93. Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

94. Schwartz, W. A., et al. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Volume I: Carbon Black Manufacturing by the Furnace Process. EPA-450/3-73-006a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 116 pp.

95. Standard for Metric Practice. ANSI/ASTM Designation E 380-76$^{\varepsilon}$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

APPENDIX A[a]

STORAGE TANKAGE CALCULATIONS

The procedures for calculating the storage capacities of the tankage needed by a representative cumene peroxidation plant and the emissions from storage tanks are outlined in this section.

CALCULATION OF TANK SIZE

Tankage requirements for the representative plant were determined by aggregation of the data available on tank sizes, number of tanks, and plant production (personal communication with L. B. Evans, 9 February 1976). Tank capacity was then determined.

Estimates of the tank diameters and heights were made using

$$D = 2\sqrt{\frac{C_t}{k_2 \pi h}} \qquad \text{(A-1)}$$

where D = tank diameter, ft
C_t = tank capacity, gal/tank
k_2 = conversion factor, 7.481 gal/ft^3
h = tank height, ft

This formula neglects the height under the slanted roof area.

Number of turnovers per year were found using

$$N = \frac{T}{C_t \cdot N'} \qquad \text{(A-2)}$$

where N = number of turnovers per year
T = throughput per year of the stored material, gal/yr
C_t = tank capacity, gal
N' = number of tanks

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[a] Nonmetric units in this appendix correspond to those used for these calculations during the study.

and throughput was determined by

$$T = \frac{U \cdot CAP}{W} k_3 \qquad \text{(A-3)}$$

where CAP = production capacity for the material, tons/yr
U = utilization, 0.80
W = liquid density of the chemical stored, lb/gal
k_3 = conversion factor, 2,000 lb/ton

Storage tank emissions consist of breathing and working losses from fixed-roof storage tanks, and evaporation and withdrawal losses from floating-roof storage tanks. Breathing losses are caused by daily changes in ambient temperature. Working losses are caused by filling and emptying the tanks. Evaporative losses from floating-roof storage tanks are caused by vapor leakage between the float and the tank shell at the seal. The losses are estimated by the methods described below. All losses are calculated as equivalent gasoline losses and then converted to specific petrochemical losses. The equations given below were derived in References 50, 80-83.

Procedure for Calculating Losses from Fixed-roof Storage Tanks

Step 1. Calculate the equivalent gasoline breathing loss:

$$Ly = \frac{24}{1,000}\left(\frac{P}{14.7 - P}\right)^{0.68} D^{1.73} H'^{0.51} (\Delta T)^{0.50} F_p C \qquad \text{(A-4)}$$

where L_y = equivalent gasoline breathing loss, bbl/yr
P = vapor pressure of material stored at bulk temperature, psia
D = tank diameter, ft
H' = average tank outage, ft
ΔT = average daily ambient temperature change, °F
F_p = paint factor
C = diameter factor

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(80) Evaporation Loss from Floating Roof Tanks. Bulletin 2517, American Petroleum Institute, New York, New York, February 1962. 13 pp.

(81) Evaporation Loss from Fixed Roof Tanks. Bulletin 2518, American Petroleum Institute, New York, New York, June 1962. 38 pp.

(82) Use of Variable Vapor Space Systems to Reduce Evaporation Loss. Bulletin 2520, American Petroleum Institute, New York, New York, September 1964. 14 pp.

(83) Petrochemical Loss from Storage Tanks. Bulletin 2523, American Petroleum Institute, New York, New York, September 1969. 14 pp.

The tank height was assumed to be 50 ft, 30 ft, 20 ft, or 15 ft as appropriate. The average tank outage, i.e., freeboard, was taken as one-half the height.

The average daily ambient temperature change, ΔT, was assumed to be 20°F, the national average value. The paint factor, F_p, an adjustment factor for the paint type, was assumed equal to unity, which is the value for white paint in good condition. The paint factor can be as high as 14.6 for gray surfaces.

The diameter factor, C, an adjustment factor for small tanks, is equal to unity for tanks 30 ft or larger in diameter. For smaller tanks, the value is obtained from a graph given in Reference 77 and is between 0.25 and 1.0.

Step 2. Calculate the equivalent gasoline working loss:

$$F_g = \frac{3}{10,000} PVNK_T \qquad \text{(A-5)}$$

where F_g = equivalent gasoline working loss, bbl/yr
V = tank capacity, bbl
N = number of turnovers per year
K_T = turnover factor = 1.0 for $N \leq 36$
$= \frac{180 + N}{6 N}$ for $N > 36$

Step 3. Compute total equivalent gasoline loss, L_g:

$$L_g = L_y + F_g \qquad \text{(A-6)}$$

Step 4. Equation A-6 determines the total equivalent gasoline loss, Lg. The petrochemical loss, L, can be determined by assuming that the volume of vapor lost is the same for the pertochamical in question as for gasoline, by assuming applicability of the ideal gas law, and by using the molecular weight, M, and liquid density, W, of the petrochemical and of gasoline. The ratio of the molecular weight of gasoline to its liquid density is 0.08. Therefore, the equation to compute the pertochemical loss is:

$$L = 0.08 \frac{M}{W} L_g \qquad \text{(A-7)}$$

where L = total petrochemical loss, bbl/yr
M = molecular weight of the chemical, lb/lb-mole
W = liquid density of chemical stored, lb/gal

Step 5. Calculate emission factors on the basis of phenol production from:

$$L_1 = L(42)(W) \tag{A-8}$$

$$E' = \frac{L_1}{CAP \cdot U} \tag{A-9}$$

$$E = \frac{E'}{2} \tag{A-10}$$

where L_1 = total petrochemical loss, lb/yr
CAP = production capacity for the material, ton/yr
E' = emission factor, lb/ton phenol produced
E = emission factor, g/kg phenol produced
U = utilization, 0.80

Using the above procedure and the storage tank input data shown in Table A-1, the emission data shown in Table A-2 were calculated for fixed-roof storage tanks.

TABLE A-1. FIXED-ROOF STORAGE TANK INPUT DATA FOR A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Input information	Material stored Acetophenone	 α-Methylstyrene	 Phenol
Number of tanks	1	1	4
Production capacity, tons/yr	150,000	150,000	150,000
Ambient temperature, °F	64	64	64
Average temperature change, °F	20	20	20
Molecular weight, lb/lb-mole	120.2	118.2	94.1
Liquid density, lb/gal	8.58	7.58	8.83
Vapor pressure, psia	0.01	0.08	0.10
Bulk temperature, °F	85	85	140
Tank diameter, ft	8	15	33
Tank outage, ft	7.5	10	25
Paint factor (83)	1.00	1.00	1.00
Diameter factor (83)	0.40	0.75	1.00
Turnover factor (83)	1.00	1.00	1.00
Number of turnovers per year	5	27	15
Tank volume, bbl	143	595	7,619
Tank height, ft	15	20	50

TABLE A-2. FIXED-ROOF STORAGE TANK EMISSION SUMMARY

Material stored[a]	Losses gal/yr	 lb/yr	Emission factor, g/kg phenol produced
Acetophenone	1.55	13.29	0.000055
α-Methylstyrene	63.10	477.7	0.0020
Phenol	455.6	4,023	0.017

[a] All losses and emission factors are per tank.

Procedure for Calculating Losses from Floating-roof Storage Tanks

Step 1. Calculate the equivalent gasoline evaporation loss:

$$L_y = K_t D^{1.5}\left(\frac{P}{14.7 - P}\right)^{0.7}\bar{u}^{0.7}K_s K_p \qquad \text{(A-11)}$$

where L_y = equivalent gasoline evaporation loss, bbl/yr
K_t = tank factor = 0.045 for welded tanks
= 0.13 for riveted tanks
D = tank diameter, ft
P = vapor pressure of material stored at bulk temperature, psia
$\bar{u}$ = average wind speed, mph
K_s = seal factor = 1.00 for tight fitting and post 1942 seals
= 1.33 for loose fitting and pre 1942 seals
K_p = paint factor = 1.00 for aluminum color
= 0.90 for white

Tank diameters were computed using a height of 50 ft, 30 ft, 20 ft, or 15 ft as appropriate.

Step 2. Calculate the equivalent gasoline withdrawal loss:

$$W_g = 0.000448 \frac{V'}{D} \qquad \text{(A-12)}$$

where W_g = equivalent gasoline withdrawal loss, bbl/yr
V' = volume of liquid withdrawn from tank, bbl/yr

Step 3. Compute total equivalent gasoline loss, L_g:

$$L_g = L_y + W_g \qquad \text{(A-13)}$$

Step 4. Equation A-13 determines the total equivalent gasoline loss, Lg. The petrochemical loss, L, can be determined by assuming that the volume of vapor lost is the same for the petrochemical in question as for gasoline, by assuming applicability of the ideal gas law, and by using the molecular weight, M, and liquid density, W, of the petrochemical and of gasoline. The ratio of the molecular weight of gasoline to its liquid density is 0.08. Therefore, the equation to compute the petrochemical loss is:

$$L = 0.08 \frac{M}{W} L_g \qquad \text{(A-14)}$$

where L = total petrochemical loss, bbl/yr
M = molecular weight of the chemical, lb/lb-mole
W = liquid density of stored chemical, lb/gal

Step 5. Calculate emission factors on the basis of phenol production from:

$$L_1 = L(42(W) \qquad \text{(A-15)}$$

$$E' = \frac{L_1}{CAP \cdot U} \qquad \text{(A-16)}$$

$$E = \frac{E'}{2} \qquad \text{(A-17)}$$

where L_1 = total petrochemical loss, lb/yr
CAP = production capacity, tons/yr
E' = emission factor, lb/ton phenol produced
E = emission factor, g/kg phenol produced

Using the above procedure and the storage tank input data shown in Table A-3, the emission data shown in Table A-4 were calculated for floating-roof storage tanks.

TABLE A-3. FLOATING-ROOF STORAGE TANK INPUT DATA FOR REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

	Tank identification		
Input information	Acetone	Cumene	Heavy ends
Number of tanks	4	3	1
Production capacity, tons/yr	150,000	150,000	150,000
Vapor pressure, psia (6)	3.87	0.09	0.0003
Bulk temperature, °F	76	76	100
Average wind speed, mph	10.07	10.07	10.07
Volume liquid withdrawn, bbl/yr	132,335	376,708	122,722
Liquid density, lb/gal	6.585	7.19	7.19
Molecular weight, lb/lb-mole (6)	58.1	120.2	250
Tank factor, welded (80, 83)	0.045	0.045	0.045
Seal factor, tight (80, 83)	1.00	1.00	1.00
Paint factor, white (80, 83)	0.9	0.9	0.9
Tank diameter, ft	30	58	17
Tank height, ft	50	50	30

TABLE A-4. FLOATING-ROOF STORAGE TANK EMISSIONS SUMMARY

	Losses		Emission factor,
Material stored[a]	gal/yr	lb/yr	g/kg phenol produced
Acetone	542.1	3,569	0.015
Cumene	307.4	2,207	0.0092
Heavy ends	379.2	2,723	0.011

[a] All losses and emission factors are per tank.

APPENDIX B

SPECIFICATIONS

Some commonly used specifications for acetone, phenol, cumene, acetophenone, and α-methylstyrene (5, 7, 9, 11-13) are:

Acetone:

Acetone	99.7 +%
Acidity	10 ppm (as acetic acid)
Water	0.3 wt % max.
Alcohols	15 ppm
Evaporative residue	10 ppm

Phenol, chlorination grade:

Phenol	99.9 +%
Water	200 ppm
Carbonyls	50 ppm (as mesityl oxide)

Cumene:

Cumene	99.99 +%
Butylbenzenes	500 ppm, max.
n-Propylbenzenes	1,000 ppm, max.
Ethylbenzene	1,000 ppm, max.

Acetophenone, perfume grade:

Acetophenone	99 +%
Chlorine	0
Other compounds	2 % max.

Acetophenone, technical grade:

Acetophenone	97 +%
Other compounds	3 %

α-Methylstyrene:

α-Methylstyrene	99.3 %
β-Methylstyrene	0.5 %
Cumene	0.2 %
TBC (an oxidation inhibitor)	15 ppm
Aldehydes	10 ppm, as CHO
Peroxides	3 ppm, as HO
Polymer	0 ppm

APPENDIX C

SAMPLING PROCEDURES AND EQUIPMENT

TEST SITE PREPARATION

Field sampling at plants manufacturing acetone and phenol from cumene did not require test site modifications. The emissions are organic vapors; therefore, isokinetic sampling was not required. Stainless steel sampling lines and valves were in place and accessible from platforms.

TEST FREQUENCY AND DURATION

Sampling results are based on a field sampling effort which took place over a two week period. A total of 8 HVOSS samples, 24 Tedlar bag samples, and 17 formaldehyde and other aldehyde samples were collected at two plants.

CARBON DIOXIDE, OXYGEN, CARBON MONOXIDE, LOW MOLECULAR WEIGHT HYDROCARBONS (LOWER THAN C_6), BENZENE, AND CUMENE

Samples for analysis for these compounds were collected in Tedlar bags. Analytical procedures will be described in Appendix D. Analytical Procedures, even though they were performed in the field.

HIGH MOLECULAR WEIGHT ORGANIC COMPOUNDS, TRACE ELEMENTS, AND MOISTURE

The sampling method used was a modification of the Source Assessment Sampling System (SASS) described in the Level I Environmental Assessment Procedures (84). The modified train is the HVOSS.

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(84) Hamersma, J. W., S. L. Reynolds, and R. F. Maddalene. IERL-RTP Procedures Manual: Level I Environmental Assessment. EPA-600/2-76-160a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1976. 147 pp.

The modifications consist of:

- The particulate collection and sizing devices were removed.
- The sampling valves were used rather than a probe heated to 200°C.
- The stack gas stream tested was controlled to approximately 5°C by using an equivalent condenser submerged in an ice bath. The XAD-2 resin module was maintained at approximately 5°C.
- An explosion-proof pump was substituted for the vacuum pump used in the SASS train.

A diagram of the sampling train is shown in Figure C-1.

Samples from the condenser and the XAD-2 module and the washings of those and the sample lines were analyzed for organic compounds.

The HVOSS train utilized four impingers containing solutions designed to trap volatile trace elements during testing at one emission point. The impinger order, impinger contents, and purposes of each impinger is shown in Table C-1.

TABLE C-1. HVOSS TRAIN IMPINGER SYSTEM REAGENTS

Impinger	Reagent	Quality	Purpose
1	6M H_2O_2	750 mℓ	Trap reducing gases such as SO_2 to prevent depletion of oxidative capability of trace element collecting impingers 2 and 3.
2	0.2M $(NH_4)_2S_2O_8$ + 0.02 M $AgNO_3$	750 mℓ	Collection of volatile trace elements by oxidative dissolution.
3	0.2M $(NH_4)_2S_2O_8$ + 0.02 M $AgNO_3$	750 mℓ	Collection of volatile trace element by oxidative dissolution.
4	Silica gel (color indicating)	750 g	Prevent moisture from reaching pump and dry gas test meter.

The impinger solutions used to collect trace elements were used on one test at each plant. One test for trace elements at each plant was performed at the request of the EPA Project Officer.

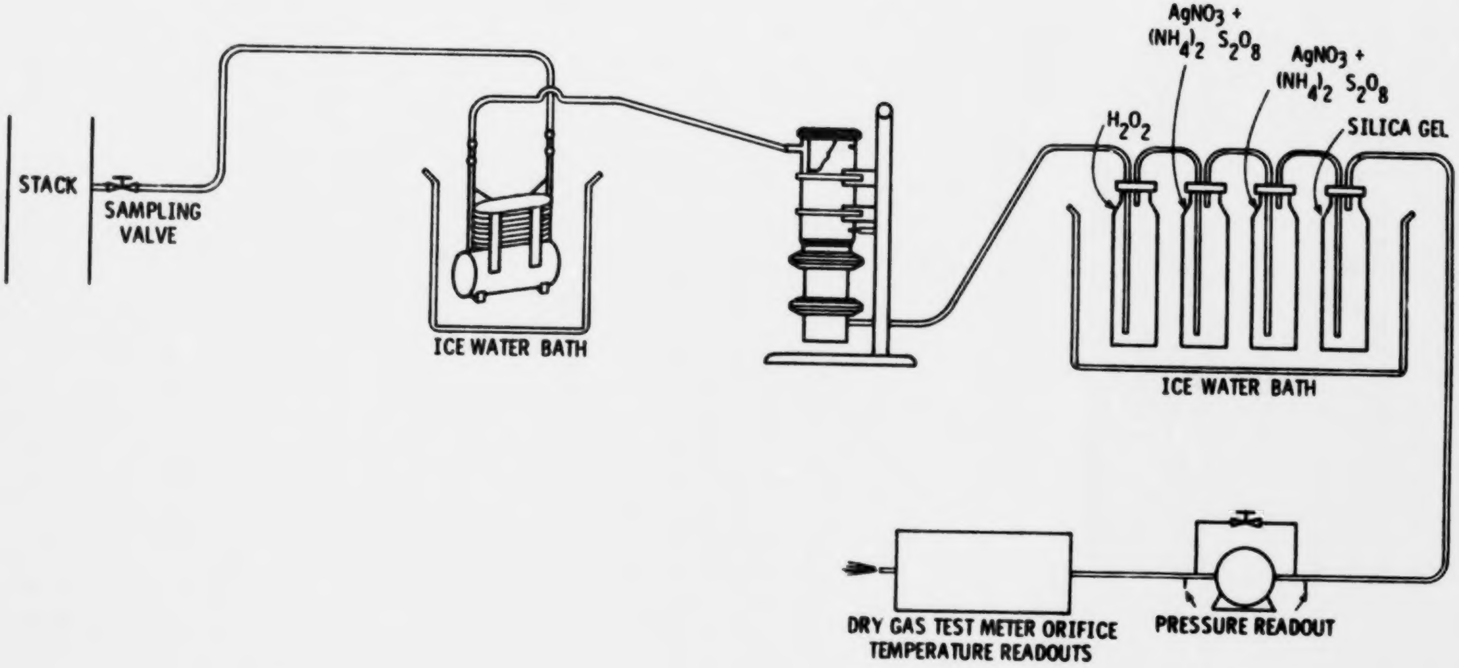
STACK
SAMPLING VALVE
ICE WATER BATH
H_2O_2
$AgNO_3 + (NH_4)_2 S_2O_8$
$AgNO_3 + (NH_4)_2 S_2O_8$
SILICA GEL
ICE WATER BATH
DRY GAS TEST METER ORIFICE TEMPERATURE READOUTS
PRESSURE READOUT

Figure C-1. High volume organic sampling system.

The remainder of the tests were carried out using the impinger system in Table C-2.

Moisture content of the stream was determined from the total amount of water collected by the HVOSS train. The train was cleaned up after each run following a modified Level I procedure.

FORMALDEHYDE AND OTHER ALDEHYDES

No standard methods have been developed for the sampling of aldehydes in stack gas emissions. The Intersociety Committee in Ambient Air Methods has developed a method for sampling aldehydes in ambient air which was modified to sample for low levels of aldehydes in stack gases. The method for ambient air involves drawing the air stream through 2 midget impingers containing 10 mℓ of 1% $NaHSO_3$ at a rate of 2 ℓ/min for 60 min and measuring the total volume of gas with a dry test meter. The minimum detectable concentration of aldehydes is 0.02 ppm by volume (85).

TABLE C-2. ALTERNATIVE HVOSS TRAIN IMPINGER SYSTEM

Impinger	Contents	Quantity	Purpose
1, 2	Water	750 mℓ	Cool the sample gas.
3	Empty	0	Spray trap, may be eliminated for low moisture content gas.
4	Silica gel	1,000 g	Prevent moisture from reaching the pump and dry gas test meter.

The method as modified for stack emissions including a sampling probe (glass) with a plug of glass wool for filtering out particulates, 2 midget impingers containing 10 mℓ of 10% $NaHSO_3$, an empty impinger, and an evacuated cylinder. As no upper limit is given for the method when used in ambient air sampling, stack gas was collected at 2 ℓ/min for periods of 15 min and 30 min. A diagram of the apparatus is shown in Figure C-2.

After sample collection, the impinger contents were transferred to a 100 mℓ sample bottle. The glass wool plug was removed and discarded. All glassware from the probe to the dry impinger was rinsed with 3 portions of 10% $NaHSO_3$, and the rinsings were added to the sample bottle.

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(85) Methods of Air Sampling and Analysis. American Public Health Association, Washington, D.C., 1972. pp. 190-198.

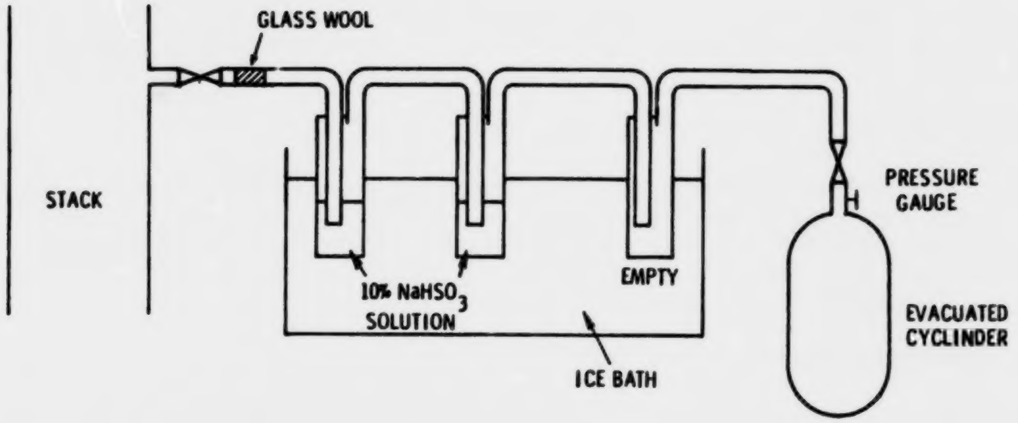
GLASS WOOL
STACK
PRESSURE GAUGE
10% NaHSO$_3$ SOLUTION
EMPTY
EVACUATED CYCLINDER
ICE BATH

Figure C-2. Diagram of sampling train for aldehydes.

APPENDIX D

ANALYTICAL PROCEDURES

Parts of the analysis program were carried out at both the field locations and at the MRC Dayton Laboratory. Field analysis included CO, CO_2, and O_2 by Orsat analysis; and C_1 to C_5 hydrocarbons, benzene, and cumene by portable GC/FID. Higher molecular weight organics (C_7 and higher), aldehyde, and formaldehyde analysis were done in the laboratory. In addition to the C_1 to C_5 hydrocarbons, benzene, and cumene field analysis, integrated gas samples were analyzed for C_1 to C_5 hydrocarbons, benzene, and cumene at the laboratory using qualitative GC/MS analysis.

CARBON DIOXIDE, CARBON MONOXIDE, AND OXYGEN

Analysis of these components was carried out in the field using the Orsat technique as specified in the Method 3 "Gas Analysis for Carbon Dioxide, Excess Air, and Dry Molecular Weight" procedure (86) and the FYRITE apparatus. Data were reported in terms of volume % for CO, CO_2, and O_2.

LOW MOLECULAR WEIGHT HYDROCARBONS

The C_1 to C_5 hydrocarbons, benzene, and cumene were sampled and analyzed at the plant site. Stack gases were collected in evacuated Tedlar bags and taken to the field laboratory. The analysis was performed using an AID portable chromatograph with a flame ionization detector (FID). The instrument was equipped with a 1.8 m by 6.4 mm stainless steel column packed with Poropak Q and was operated isothermally with a column temperature of 50°C. Standard gas mixtures of the compounds were taken to quantify the data. The data were reported as alkenes (C_1 to C_5), benzene, and cumene vppm. Qualitative GC/MS analysis was performed to corroborate the field identification.

HIGHER MOLECULAR WEIGHT ORGANIC COMPOUNDS

A flow diagram for the sample collection and preparation is shown in Figure D-1.

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(86) Method 3 - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight. Federal Register, 41(111): 23069-23070, 1976.

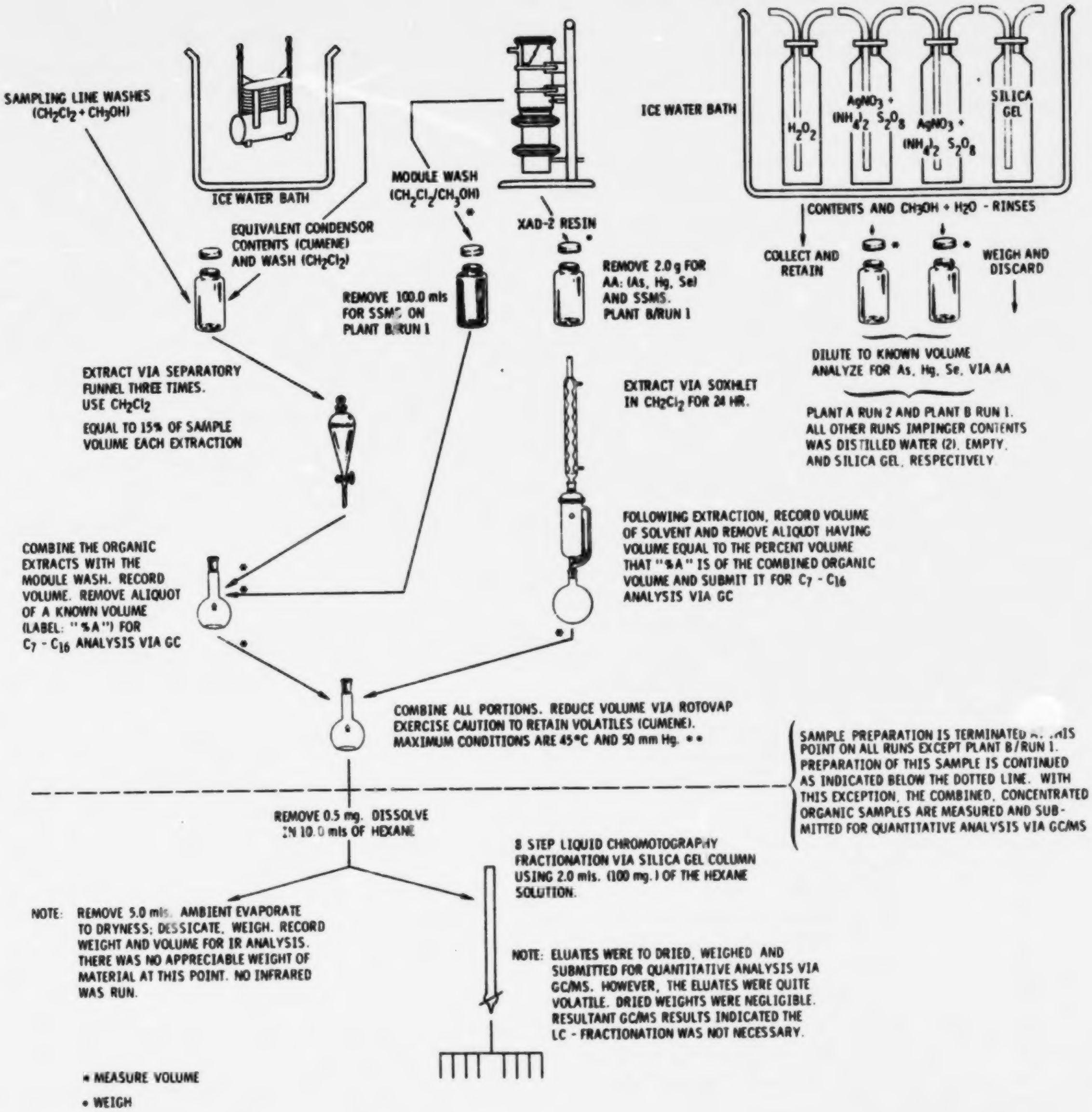
SAMPLING LINE WASHES ($CH_2Cl_2 + CH_3OH$)
ICE WATER BATH
EQUIVALENT CONDENSOR CONTENTS (CUMENE) AND WASH (CH_2Cl_2)
MODULE WASH (CH_2Cl_2/CH_3OH) *
XAD-2 RESIN *
ICE WATER BATH
H_2O_2
$AgNO_3$ + $(NH_4)_2$ S_2O_8
$AgNO_3$ + $(NH_4)_2$ S_2O_8
SILICA GEL
CONTENTS AND CH_3OH + H_2O - RINSES
COLLECT AND RETAIN
WEIGH AND DISCARD
REMOVE 100.0 mls FOR SSMS ON PLANT B/RUN 1
REMOVE 2.0 g FOR AA: (As, Hg, Se) AND SSMS. PLANT B/RUN 1
DILUTE TO KNOWN VOLUME ANALYZE FOR As, Hg, Se, VIA AA
PLANT A RUN 2 AND PLANT B RUN 1. ALL OTHER RUNS IMPINGER CONTENTS WAS DISTILLED WATER (2), EMPTY, AND SILICA GEL, RESPECTIVELY.
EXTRACT VIA SEPARATORY FUNNEL THREE TIMES. USE CH_2Cl_2
EQUAL TO 15% OF SAMPLE VOLUME EACH EXTRACTION
EXTRACT VIA SOXHLET IN CH_2Cl_2 FOR 24 HR.
FOLLOWING EXTRACTION, RECORD VOLUME OF SOLVENT AND REMOVE ALIQUOT HAVING VOLUME EQUAL TO THE PERCENT VOLUME THAT "%A" IS OF THE COMBINED ORGANIC VOLUME AND SUBMIT IT FOR C_7 - C_{16} ANALYSIS VIA GC
COMBINE THE ORGANIC EXTRACTS WITH THE MODULE WASH. RECORD VOLUME. REMOVE ALIQUOT OF A KNOWN VOLUME (LABEL: "%A") FOR C_7 - C_{16} ANALYSIS VIA GC
COMBINE ALL PORTIONS. REDUCE VOLUME VIA ROTOVAP EXERCISE CAUTION TO RETAIN VOLATILES (CUMENE). MAXIMUM CONDITIONS ARE 45°C AND 50 mm Hg. * •
SAMPLE PREPARATION IS TERMINATED AT THIS POINT ON ALL RUNS EXCEPT PLANT B/RUN 1. PREPARATION OF THIS SAMPLE IS CONTINUED AS INDICATED BELOW THE DOTTED LINE. WITH THIS EXCEPTION, THE COMBINED, CONCENTRATED ORGANIC SAMPLES ARE MEASURED AND SUBMITTED FOR QUANTITATIVE ANALYSIS VIA GC/MS
REMOVE 0.5 mg. DISSOLVE IN 10.0 mls OF HEXANE
8 STEP LIQUID CHROMOTOGRAPHY FRACTIONATION VIA SILICA GEL COLUMN USING 2.0 mls. (100 mg.) OF THE HEXANE SOLUTION.
NOTE: REMOVE 5.0 mls. AMBIENT EVAPORATE TO DRYNESS; DESSICATE. WEIGH. RECORD WEIGHT AND VOLUME FOR IR ANALYSIS. THERE WAS NO APPRECIABLE WEIGHT OF MATERIAL AT THIS POINT. NO INFRARED WAS RUN.
NOTE: ELUATES WERE TO DRIED, WEIGHED AND SUBMITTED FOR QUANTITATIVE ANALYSIS VIA GC/MS. HOWEVER, THE ELUATES WERE QUITE VOLATILE. DRIED WEIGHTS WERE NEGLIGIBLE. RESULTANT GC/MS RESULTS INDICATED THE LC - FRACTIONATION WAS NOT NECESSARY.
* MEASURE VOLUME
• WEIGH

Figure D-1. Flow diagram for sample collection and preparation at plants manufacturing acetone and phenol from cumene.

The XAD-2 resin was Soxhlet extracted for 24 hr with pentane. The volume was measured and a 1 mℓ to 10 mℓ portion was removed for GC analysis of the C_7 to C_{16} hydrocarbons. The remaining solution was stored for later combination with the other samples from the run. For one run at each plant, 2 g of resin were removed prior to extraction for elemental analysis.

The condensate and the sample line washes from the run were extracted with methylene chloride; this extract was then combined with the methylene chloride rinse of the module. The volumes of these solutions were measured and a portion equal to the percentage of the portion removed from the pentane extract of the XAD-2 resin extraction was removed for C_7 to C_{16} analysis. The remaining solution, representing the same percentage of the total as the remaining pentane solution of the extraction total, was combined with the pentane extraction solution. The resulting solution was reduced in volume in a rotovap with maximum conditions of 45°C and 50 mm Hg. One run was evaporated to dryness to obtain a residue for IR analysis. There was no residue. Furthermore, that sample was fractionated using column liquid chromatography into eight fractions of varying polarity using the solvent mixtures shown in Table D-1. Each of the fractions were then analyzed by GC/MS to identify and quantify the components. Infrared spectra of the fractions were not required. Only two fractions contained compounds in the GC/MS analysis. No other runs were fractionated using this information as a basis for going to direct GC/MS analysis.

TABLE D-1. SOLVENTS USED IN LIQUID CHROMATOGRAPHIC SEPARATIONS

Fraction number	Solvent composition
1	Pentane
2	20% Methylene chloride in pentane
3	50% Methylene chloride in pentane
4	Methylene chloride
5	5% Methanol in methylene chloride
6	20% Methanol in mehtylene chloride
7	50% Methanol in methylene chloride
8	5/70/30, Concentration HCl/methanol/methylene chloride

FORMALDEHYDE

Formaldehyde was collected in impingers containing a 10% $NaHSO_3$ solution as described in Apprendix C. The analysis method was patterned after Tentative Method 110 included in Appendix E, which was proposed by the Interscience Committee.

Formaldehyde is measured in an aliquot of the collection medium by the chromatropic acid procedure. After reaction with chromatropic acid and sulfuric acid, the transmittance was read at 580 nm. A blank containing 2 mℓ of 10% bisulfite was employed to set the 100% transmittance reading and a standard curve was generated employing known sodium formaldehyde bisulfite solutions equivalent to 1 μg, 5 μg, and 7 μg formaldehyde/mℓ.

OTHER ALDEHYDES

C_2 to C_5 aldehydes were collected in impingers containing a 10% $NaHSO_3$ solution as described in Appendix C. The analysis method was patterned after Tentative Method 110 Appendix E as proposed by the Interscience Committee (85).

The aldehydes were measured using GC/FID. The GC column was 4 m x 3 mm stainless steel, packed with 15% by weight of carbowax 20M on chromasorb, 60 to 80 mesh, followed by 1.7 m x 3 mm stainless steel, packed with uncondinonylphthalate on firebrick. Retention times for the various species, under the conditions given in Appendix E are presented in Table D-2.

TABLE D-2. RETENTION TIMES FOR ALDEHYDES, KETONES, ALCOHOLS, AND ESTERS

Reprinted from Methods of Air Sampling and Analysis by permission of the American Public Health Association.

Compound	Retention time, min
Acetaldehyde	3.5
Propionaldehyde	4.6
Acetone	5.1
Isobutylaldehyde	5.5
Methyl alcohol	6.1
Ethyl alcohol	6.7
Isopropyl alcohol	6.7
Ethyl acetate	7.0
n-Butylaldehyde	7.1
Methyl ethyl ketone	7.7
Isopentanol	12.0
Crotonaldehyde	14.0

TRACE ELEMENT ANALYSIS

Analysis of trace element composition was performed on the XAD-2 resin, the XAD-2 resin module wash, and the contents of impingers 2 and 3. Atomic absorption (AA) was used to analyze arsenic, mercury, and selenium in the impingers while SSMS by CDM/Accu Labs quantified 69 elements including: uranium, thorium, bismuth, lead, thallium, mercury, gold, platinum, iridium, osmium, tungsten, tantalum, hafnium, lutetium, ytterbium, thulium,

erbium, holmium, dysprosium, terbium, gadolinium, europium, samarium, neodymium, praseodymium, cerium, lanthanum, barium, cesium, iodine, tellurium, antimony, tin, cadmium, silver, palladium, rhodium, ruthenium, molybdenum, niobium, zirconium, yttrium, strontium, rubidium, bromine, selenium, arsenic, germanium, gallium, zinc, copper, nickel, cobalt, iron, manganese, chromium, vanadium, titanium, scandium, calcium, potassium, chlorine, sulfur, phosphorus, silicon, aluminum, magnesium, sodium, and fluorine. SSMS is a semiquantitative method whose accuracy in this use is +200%, -100%.

All solid samples were digested before analysis using the acid digestion Parr bomb technique originally developed by Bernas and modified by Hartstein for trace metal analysis of coal dust by AA (87, 88). This method employs the Parr 4145 Teflon-lined bomb and involves digestion of the samples in fuming nitric acid at 150°C. Sample solutions produced by acid digestion were first diluted with distilled water to reduce acid concentration to approximately 2% and then submitted for analysis.

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(87) Bernas, B. A New Method for Decomposition and Comprehensive Analysis of Silicates by Atomic Absorption Spectrometry. Analytical Chemistry, 40(11):1682-1686, 1968.

(88) Hartstein, A. M., R. W. Freedman, and D. W. Platter. Novel Wet-Digestion Procedure for Trace-Metal Analysis of Coal by Atomic Absorption. Analytical Chemistry, 45(3);611-614, 1973.

APPENDIX E

SAMPLING AND ANALYSIS METHODS FOR FORMALDEHYDE AND ALDEHYDES (85)

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INTERSOCIETY COMMITTEE

110

TENTATIVE METHOD OF ANALYSIS FOR LOW MOLECULAR WEIGHT ALIPHATIC ALDEHYDES IN THE ATMOSPHERE

43501–01–71T

1. Principle

Formaldehyde, acrolein and low molecular weight aldehydes are collected in 1 per cent $NaHSO_3$ solution in midget impingers. Formaldehyde is measured in an aliquot of the collection medium by the chromotropic acid procedure, acrolein by a modified mercuric-chloride-hexylresorcinol procedure, and C_2–C_5 aldehydes by a gas chromatographic procedure. The method permits the analysis of all C_1-C_5 aldehydes in a sample (1).

The sampling procedure is not applicable for the determination of alcohols, esters or ketones in atmospheric samples, since bisulfite does not efficiently collect these materials. However, should some of these compounds be present in the atmosphere, their presence may be indicated by the appearance of peaks corresponding to their retention times in the chromatograms. The retention times for several of these compounds are shown along with the aldehydes in Table 1.

2. Range and Sensitivity

At sampling rates of 2 liters/min over a 1 hr period, the following minimum concentrations can be determined:

CH_2O:	0.02 ppm
CH_3CHO:	0.02 ppm
CH_3CH_2CHO:	0.03 ppm
$(CH_3)_2CHCHO$:	0.03 ppm
$CH_2 = CHCHO$:	0.01 ppm

Shorter sampling periods are permissible for higher concentrations.

3. Interferences

3.1 *Formaldehyde.*

3.1.1 The chromotropic acid procedure has very little interference from other aldehydes. Saturated aldehydes give less than 0.01 per cent positive interference, and the unsaturated aldehyde acrolein results in a few per cent positive interference. Ethanol and higher molecular weight alcohols and olefins in mixtures with formaldehyde are negative interferences. However, concentrations of alcohols in air are usually much lower than formaldehyde concentrations and, therefore, are not a serious interference.

3.1.2 Phenols result in a 10–20 per cent negative interference when present at an 8:1 excess over formaldehyde. They are, however, ordinarily present in the atmosphere at lesser concentrations than formaldehyde and, therefore, are not a serious interference.

3.1.3 Ethylene and propylene in a 10:1 excess over formaldehyde result in a 5–10 per cent negative interference and 2-methyl-1, 3-butadiene in a 15:1 excess over formaldehyde showed a 15 per cent negative interference. Aromatic hydrocarbons also constitute a negative interference. It has recently been found that cyclohexanone causes a bleaching of the final color.

3.2 *Acrolein.*

3.2.1 There is no interference in the acrolein determination from ordinary quantities of sulfur dioxide, nitrogen dioxide, ozone and most organic air pollutants. A slight interference occurs

Table 1. Retention Times for Aldehydes, Ketones, Alcohols and Esters*

Compound	Time, Retention minutes
Acetaldehyde	3.5
Propionaldehyde	4.6
Acetone	5.1
Isobutylraldehyde	5.5
Methyl alcohol	6.1
Ethyl alcohol	6.7
Isopropyl alcohol	6.7
Ethyl acetate	7.0
n-Butyraldehyde	7.1
Methyl-ethyl ketone	7.7
Isopentanal	12.0
Crotonaldehyde	14.0

* Flow rate, temperature and conditions described in text.

from dienes: 1.5 per cent for 1,3-butadiene and 2 per cent for 1, 3-pentadiene. The red color produced by some other aldehydes and undetermined materials does not interfere in spectrophotometric measurement.

4. Precision and Accuracy

Known standards can be determined to within ±5 per cent of the true value. No data are available on precision and accuracy for atmospheric samples.

5. Apparatus

5.1 *Absorbers*—All glass standard midget impingers are acceptable. A train of 2 bubblers in series is used.

5.2 *Air Pump*—A pump capable of drawing at least 2 liters of air/min for 50 min through the sampling train is required.

5.3 *Air Metering Device*—Either a limiting orifice of approximately 2 liters/min capacity or a glass flow meter can be used. Cleaning and frequent calibration are required if a limiting orifice is used.

5.4 *Spectrophotometer*—This instrument should be capable of measuring the developed colors at 605 nm and 580 nm. The absorption bands are rather narrow, and thus a lower absorptivity may be expected in a broad-band instrument.

5.5 *Gas Chromatograph* with hydrogen flame detector and injection port sleeve (Varian 1200 or equivalent).

5.6 *Boiling Water Bath.*

6. Reagents

6.1 *Determination of formaldehyde.*

6.1.2 **Sodium formaldehyde bisulfite** (E.K. P6450).

6.1.3 **Chromotropic acid sodium salt, EK P230. 0.5 per cent in water.** Filter just before using. Stable for one week if kept refrigerated.

6.1.4 **Sulfuric acid.** Concentrated reagent grade.

6.2 *Determination of Acrolein.*

6.2.1 **$HgCl_2$-4-hexylresorcinol.** 0.30 g $HgCl_2$ and 2.5 g 4 hexylresorcinol are dissolved in 50 ml 95 per cent ethanol. (Stable at least 3 weeks if kept refrigerated.)

6.2.2 **TCAA.** To a 1 lb bottle of trichloracetic acid add 23 ml distilled water and 25 ml 95 per cent ethanol. Mix until all the TCAA has dissolved.

6.3 *Collection Medium*—Sodium bisulfite, 1 per cent in water.

7. Procedure

7.1 *Collection of Samples*—Two midget impingers, each containing 10 ml of 1 per cent $NaHSO_3$ are connected in series with Tygon tubing. These are followed by and connected to an empty impinger (for meter protection) and a dry test meter and a source of suction. During sampling the impingers are immersed in an ice bath. Sampling rate of 2 liters/min should be maintained. Sampling duration will depend on the concentration of aldehydes in the air. One hour sampling time at 2 liters/min is adequate for ambient concentrations.

After sampling is complete, the im

pingers are disconnected from the train, the inlet and outlet tubes are capped, and the impingers stored in an ice bath or at 6 C in a refrigerator until analyses are performed. Cold storage is necessary only if the acrolein determination cannot be performed within 4 hr of sampling.

7.2 *Analysis of Samples* (each impinger is analyzed separately).

7.2.1 **Formaldehyde (1) (2).** Transfer a 2-ml aliquot of the absorbing solution to a 25-ml graduated tube. Add 0.2 ml chromotropic acid, and then, cautiously, 5.0 ml concentrated sulfuric acid. Mix well. Transfer to a boiling water bath and heat for 15 minutes. Cool the samples and add distilled water to the 10-ml mark. Cool, mix and transfer to a 16-mm cuvette, reading the transmittance at 580 nm. A blank containing 2 ml of 1 per cent sodium bisulfite should be run along with the samples and used for 100 per cent T setting. From a standard curve read micrograms of formaldehyde.

7.2.2 **Acrolein (1) (3).** To a 25-ml graduated tube add an aliquot of the collected sample in bisulfite containing no more than 30 μg acrolein. Add 1 per cent sodium bisulfite (if necessary) to a volume of 4.0 ml. Add 1.0 ml of the $HgCl_2$-4-hexylresorcinol reagent and mix. Add 5.0 ml of TCAA reagent and mix again. Insert in a boiling water bath for 5–6 min, remove, and set aside until tubes reach room temperature. Centrifuge samples at 1500 rpm for 5 min to clear slight turbidity. One hour after heating, read in a spectrophotometer at 605 nm against a bisulfite blank prepared in the same fashion as the samples.

7.2.3 **C_2-C_5 Aldehydes (1).**

7.2.3.1 *Analytical column*—12′ x ⅛″ stainless steel packed with 15 per cent w/w Carbowax 20 M on Chromosorb, 60–80 mesh, followed by 5′ x ⅛″ stainless steel Uncondinonylphthalate on firebrick, 100–200 mesh, prepared as follows: Ucon 50-HB-2000, 1.5 g, and 1.4 g of dinonylphthalate are dissolved in chloroform and added to 13 g of firebrick. The solvent is evaporated at room temperature and the column packed in the usual manner.

7.2.3.2 *Injection port sleeve*—The inlet of the injection port contains a glass sleeve packed with solid Na_2CO_3. The Na_2CO_3 is held in place with glass wool plugs.

7.2.3.3 *Conditions*—

Injection port temperature, 160–170 C
Column temperature, 105 C
Detector temperature, 200 C
Nitrogen carrier gas flow rate, 14 ml/min
Hydrogen flow rate, 20 ml/min
Combustion air flow rate, 400/min

7.2.3.4 *Procedure*—A 4 μl sample of the bisulfite collection solution is injected into the packed sleeve at the injection port and the chromatogram is recorded. Table 1 shows the relative retention times for a series of aldehydes and ketones in the C_2-C_5 range.

8. Calibration

8.1 *Formaldehyde.*

8.1.1 **Preparation of standard curve.** To a 1 liter volumetric flask add 0.4466 g sodium formaldehyde bisulfite and dilute to volume. This solution contains 0.1 mg formaldehyde per milliliter. Dilute to obtain standard solutions containing 1, 3, 5 and 7 μg formaldehyde per milliliter. Treat 2-ml aliquots as described in the procedure for color development. Read each at 580 nm after setting instrument at 100 per cent T with the blank. Using semilog paper, graph the respective concentrations vs. transmittance.

8.2 *Acrolein.*

8.2.1 **Preparation of standard curve.** To 250 ml of 1 per cent sodium bisulfite add 4.0 μl freshly distilled acrolein. This yields a standard containing 13.4 μg/ml. To a series of tubes add

0.5, 1.0, 1.5, and 2.0 ml of standard. Adjust the volumes to 4.0 ml with 1 per cent bisulfite and develop color as described above. Plot data on semi-log paper.

8.3 *C_2–C_5 Aldehydes.*

8.3.1 **Calibration.** A mixed standard of C_2–C_5 aldehydes and ketones is prepared as follows:

a. Acetaldehyde-bisulfite solution: 0.336 g $CH_3\ CHO \cdot NaHSO_3$ (EK 791) is dissolved in 1 liter of 1 per cent $NaHSO_3$. This gives a solution containing 100 μg/ml acetaldehyde.

b. To 10.0 ml of the above solution are added 40.0 ml of 1 per cent $NaHSO_3$, and 8 μl of a mixture of equal volumes of propanal, isobutanal, butanal, isopentanal, pentanal crotonaldehyde, acetone and butanone.

The final solution contains 20 μg/ml acetaldehyde and 0.02 μl of each of the C_2–C_5 aldehydes and ketones per milliliter. Four microliters of the standard are injected into the glass sleeve in the injection port of the chromatograph as described in the procedure, and the chromatogram is recorded.

9. Calculations

(1.23 μg formaldehyde = 1μl (vol) at 25 C and 760 Torr)

9.1 *Formaldehyde*—ppm formaldehyde (CH_2O) =

$$\frac{\text{total micrograms of } CH_2O \text{ in sample}}{1.23 \times \text{sample volume in liters}}$$

9.2 *Acrolein*—

(2.3 μg acrolein = 1.0 μl (vol) acrolein)

$$\text{ppm} = \frac{\text{total } \mu\text{g of acrolein in sample}}{2.3 \times \text{sample volume in liters}}$$

9.3 *Aldehydes*—Calculation of unknown sample concentration is made on the basis of comparative peak heights between standards and unknowns.

10. Effect of Storage

After sampling is complete, collection media are stored in an ice bath or refrigerator at 6 C. Cold storage is necessary only if acrolein is to be determined. Under cold storage conditions, analyses can be performed within 48 hr with no deterioration of collected samples.

11. References

1. Levaggi, D. A., and Feldstein, M. The Determination of Formaldehyde, Acrolein and Low Molecular Weight Aldehydes in Industrial Emissions on a Single Collected Sample. JAPCA. 20:312, 1970.
2. Tentative Method for the Determination of Formaldehyde in the Atmosphere, H.L.S. 7:87, 1970.
(See Part II: Item 111, p. 194).
3. Tentative Method for the Analysis of Acrolein Content of the Atmosphere, H. L. S. 7:179, 1970.
(See Part II: Item 109, p. 187).

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APPENDIX F

AVERAGE EMISSION FACTORS UNCONTROLLED AND CONTROLLED FROM THE PEROXIDATION VENT AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Table F-1 lists the average emission factors uncontrolled and controlled from the peroxidation vent at a plant manufacturing acetone and phenol from cumene.

TABLE F-1. AVERAGE EMISSION FACTORS UNCONTROLLED AND CONTROLLED FROM THE PEROXIDATION VENT AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Material emitted	Emission factor, g/kg phenol produced, ±95% confidence level bound[a,b]	
	Inlet to control device	Outlet from control device
Criteria pollutants:[c]		
Total nonmethane hydrocarbons[d]	9.6	1.8
Chemical substances:		
Acetaldehyde	$<0.0013 \, ^{+320\%}_{-100\%}$	$<0.0021 \, ^{+320\%}_{-100\%}$
Acetone	$2.4 \, ^{+840\%}_{-100\%}$	$0.60 \, ^{+860\%}_{-100\%}$
Acetophenone	<0.0014	<0.0086
Benzene[e]	0.22 ± 16%	0.20 ± 9.4%
2-Butanone	$0.089 \, ^{+200\%}_{-100\%}$	$0.050 \, ^{+300\%}_{-100\%}$
2-Butenal	$<0.0029 \, ^{+320\%}_{-100\%}$	$<0.0055 \, ^{+460\%}_{-100\%}$
t-Butylbenzene	<0.0085	<0.0022
Cumene	$6.9 \, ^{+240\%}_{-100\%}$	$<0.86 \, ^{+170\%}_{-100\%}$
Dimethylstyrene	<0.0005	0.00005
Ethylbenzene	0.027	0.00042
Formaldehyde	$0.038 \, ^{+460\%}_{-100\%}$	$0.0010 \, ^{+520\%}_{-100\%}$
2-Hydroxy-2-phenylpropane	<0.0019	<0.0009
α-Methylstyrene[f]	<0.0005	<0.0001
Naphthalene	<0.0005	<0.0001
Propanal	$<0.0017 \, ^{+220\%}_{-100\%}$	$<0.0011 \, ^{+240\%}_{-100\%}$
Elements:		
Arsenic	<0.0000006 ± 71%[g]	-[h]
Barium	$<0.0002 \, ^{+350\%}_{-100\%}$[i]	-[h]
Calcium	$<0.0006 \, ^{+210\%}_{-100\%}$[i]	-[h]
Chlorine	$<0.0002 \, ^{+400\%}_{-100\%}$[i]	-[h]
Fluorine	$0.0002 \, ^{+400\%}_{-100\%}$[i]	-[h]
Magnesium	$<0.00007 \, ^{+280\%}_{-100\%}$[i]	-[h]

(continued)

TABLE F-1 (continued)

Material emitted	Emission factor, g/kg phenol produced, ±95% confidence level bound[a,b]	
	Inlet to control device	Outlet from control device
Manganese	0.000005 $^{+400\%}_{-100\%}$[i]	–[h]
Phosphorus	<0.0002 $^{+400\%}_{-100\%}$[i]	–[h]
Potassium	<0.0006 $^{+400\%}_{-100\%}$[i]	–[h]
Sodium	<0.002 $^{+400\%}_{-100\%}$[i]	–[h]
Sulfur	<0.0006 $^{+260\%}_{-100\%}$[i]	–[h]
Titanium	<0.00005 $^{+340\%}_{-100\%}$[i]	–[h]

Note.—Values given as less (<) are the amount in the sample only, because the amount in the in the blank was either greater than the amount in the sample, or not detected.

[a] The percent error bound for the average emission factor is the root mean square of the 95% confidence level error bounds at Plant A and Plant B. It is calculated by

$$\pm\% = \frac{\sqrt{\Sigma_A^2 + \Sigma_B^2}}{\left(\frac{\bar{x}_A + \bar{x}_B}{2}\right)} 100$$

and $\Sigma = \frac{s \cdot t}{\sqrt{n}}$

[b] Materials without the 95% confidence level error bound were tested once; therefore, no error bound can be determined.

[c] No particulates, nitrogen oxides (NO_x), sulfur oxides (SO_x), or carbon monoxide are emitted.

[d] The total nonmethane hydrocarbon emission factor is the sum of the methane equivalent emission factors, based on carbon content, for the C_2 through C_{16} materials determined by gas chromatographic (GC) analysis. The total nonmethane hydrocarbon emission factor is not the sum of emission factors for all nonmethane organic materials.

[e] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

[f] The GC/MS analysis does not distinguish among forms. It was assumed to be the α form.

[g] The error bound determined from the accuracy for atomic absorption (AA).

[h] Not sampled.

[i] The error bound determined from the accuracy for spark source mass spectrometry (SSMS).

APPENDIX G

AVERAGE EMISSION FACTORS FOR THE CLEAVAGE SECTION VENTS (COMBINED) AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1976 AND 1977

Table G-1 lists the average emission factors for the cleavage section vents (combined) at a plant manufacturing acetone and phenol from cumene in 1976 and 1977.

TABLE G-1. AVERAGE EMISSION FACTORS FOR THE CLEAVAGE SECTION VENTS (COMBINED) AT A PLANT MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1976 and 1977

Material emitted	Emission factor, g/kg phenol produced[a]
Criteria pollutants:[b]	
Total nonmethane hydrocarbons[c]	0.17
Chemical substances:	
Acetone	0.0000060
Acetophenone	0.0000044
Benzene[d]	0.000031
2-Butanone	0.0000018
2-Butenal	0.000000085
t-Butylbenzene	0.000023
Cumene	0.14
Ethylbenzene	0.0000050
Formaldehyde	<0.00000026
2-Hydroxy-2-phenylpropane	0.0000034
Isopentanal	0.00000085

Note.—Values given as less than are the amount in the sample only, because the amount in the blank was either greater than the amount in the sample or not detected.

[a] Calculation of the 95% confidence level error bounds is not possible because some materials were tested once and because data obtained from industry and used to form the average emission factors do not have error bounds.

[b] No particulates, NO_x, SO_x, or carbon monoxide are emitted.

[c] The total nonmethane hydrocarbon emission factor is the sum of the methane equivalent emission factors, based on carbon content, for all nonmethane organic materials.

[d] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

APPENDIX H

REPORTED EMISSIONS INFORMATION

Responses to the Air Products and Chemicals, Inc., Houdry Division survey (in support of EPA Contract 68-02-0255) have been analyzed and are presented in Tables H-1 to H-8, (personal communication with L. B. Evans, 9 February 1976). These emission factors were not used in this report. The reported information is, in some instances, out of date because of plant shutdowns, modifications, and expansions since the data were reported in 1972. The accuracy and precision of the results are also limited by wide variations in the amount of data reported and the methods of determination. The methods of determination reported in the survey responses are material balances or engineering estimates (56%), non EPA approved sampling methods (28%), and unknown sampling methods (16%). The emission factors determined from the survey responses are higher than the emission factors determined from sampling and recent industry contact.

More recent emission information was obtained from EPA on two plants. Table H-9 presents the information obtained on the Georgia Pacific Corp., plant at Plaquemine, Louisiana (personal communication with Vernon C. Parker, 10 March 1976). Emission factors from this source were used in this report. Also, information was obtained on the Clark Oil and Refining plant at Blue Island, Illinois, (personal communication with Philip J. Mole, 10 March 1976). There are no reported pollutant emissions. All process vents are connected to an afterburner.

TABLE H-1. REPORTED EMISSIONS INFORMATION FOR PLANT 1

Emission point	Emission	Emission factor, g/kg phenol produced	Determination method	Emission control	Emission height, m
Peroxidation vent			Cumene condensed.	Carbon adsorbers.	
	Cumene	3.6			
	Hydrocarbons[a]	4.3			
Steam jet vent					15.2
Vent					21.3
Steam jet vent					22.9
Vent					22.9
Vent					22.9
Steam jet vent					15.2
Vent					15.2
Vent					22.9
Storage tank vents				Conservation vents or none.	
Fugitive emissions	Undetermined				

Note.—Blanks indicate no information reported.

[a] Hydrocarbon emission factor is based on the nonmethane equivalent:

$$MEEF = \frac{E}{M_c} C_c M_m$$

where MEEF = methane equivalent emission factor, g/kg phenol produced
E = material emission factor, g/kg phenol produced
M_c = material molecular weight, g/g-mole
C_c = g moles of carbon that a gram of material contains
M_m = molecular weight of methane, 16.04 g/g-mole

TABLE H-2. REPORTED EMISSIONS INFORMATION FOR PLANT 2

Emission point	Emission	Emission factor, g/kg phenol produced	Determination method	Emission control	Emission height, m
Incineration stack	NO_x[a]	2.3	Sampled.	Incinerator.	16.8
Storage tank vents				Floating roofs and none.	
Fugitive emissions	None but minor leakages may occur.				

Note.—Blanks indicate no information reported.

[a] Incinerator not operating when reported; absorbers emit 0.26 g/kg phenol of cumene (or 0.32 g/kg phenol of total nonmethane hydrocarbons). Nonmethane hydrocarbon emission factors are the sum of the nonmethane equivalnet emission factor, based on carbon content for all nonmethane organic materials.

TABLE H-3. REPORTED EMISSIONS INFORMATION FOR PLANT 3

Emission point	Emission	Emission factor, g/kg phenol produced	Determination method	Emission control	Emission height, m
Spent off gas vent			GLC[a] analysis of acetone used to scrub gas sample.	Carbon adsorbers.	26.2
	Cumene	12			
	Formaldehyde	1.9			
	Hydrocarbons[b]	15			
Concentration vent			Gas chromatograph analysis.	Condenser.	23.2
	Cumene	0.089			
	Formaldehyde	0.0083			
	Benzene	0.0043			
	Toluene	0.0043			
	Ethylbenzene	0.0010			
	Hydrocarbons	0.12			
Cleavage vent			Material balance.	Condenser.	23.2
	Acetone	0.28			
	Hydrocarbons	0.23			
Acetone topping vent			GLC analysis of liquid used to estimate vapor composition.	None.	26.2
	Acetone	6.0			
	Acetaldehyde	0.31			
	Hydrocarbons	5.2			
Acetone tower vent			Material balance.	None.	26.2
α-Methylstyrene vent			GLC analysis of liquid used to estimate vapor composition.	None.	21.3
	Cumene	0.21			
	Toluene	0.043			
	Ethylbenzene	0.31			
	Mesityl oxide	0.069			
	Hydrocarbons	0.75			
Storage tank vents				Condensers, conservation vents, and none.	
Fugitive emissions	Minor.				

Note.—Blanks indicate no information reported.

[a] Gas/liquid chromatography.

[b] Hydrocarbon emission factor is the sum of the methane equivalent emission factors, based on carbon content, for all nonmethane organic materials.

TABLE H-4. REPORTED EMISSIONS INFORMATION FOR PLANT 4

Emission point	Emission	Emission factor, g/kg phenol produced	Determination method	Emission control	Emission height, m
Peroxidation vent			Engineering estimate.	Condenser.	21.3
	Cumene	1.6			
	Formaldehyde	2.6			
	Benzene	1.2			
	Hydrocarbons[a]	4.8			
Cumene hydroperoxide wash and surge tank vent			Engineering estimate.	Condenser.	9.1
	Cumene	0.27			
	Hydrocarbons	0.32			
Cumene stripper vent				Vent condenser.	12.2
Cleavage vent	Minor			Condenser.	
Wash vent	Minor			None.	
Phenol-acetone still	Minor			Condenser.	
Acetone topping column vent				Condenser	24.4
	Acetone	0.97			
	Acetaldehyde	0.75			
	Hydrocarbons	1.35			
Acetone column	Minor			Condenser.	
Separation column vent	Minor			None.	
Dewatering column vent	Minor			None.	
Storage tank vents				Floating roofs, N_2 blankets, conservation vents, and none.	
Fugitive emissions	None.				

Note.—Blanks indicate no data reported.

[a] Hydrocarbon emission factors are the sum of the nonmethane equivalent emission factors, based on carbon content, for all nonmethane organic materials.

TABLE H-5. REPORTED EMISSIONS INFORMATION FOR PLANT 5

Emission point	Emission	Emission factor, g/kg phenol produced	Determination method	Emission control	Emission height, m
Peroxidation vent				Recovery system.	13.7
Concentration and cleavage vent					14.4
Acetone fractionation vent					24.4
Cumene column vent					32.0
α-Methylstyrene column vent					29.0
Phenol column vent					19.8
Residue stripping column vent					19.8
Acetone vent					24.4
Acetone concentration vent					28.3
Batch still vent					29.0
Storage tank vents				None.	
Fugitive emissions	Total unknown.				

Note.—Blanks indicate no information reported.

TABLE H-6. REPORTED EMISSIONS INFORMATION FOR PLANT 6

Emission point	Emission	Emission factor, g/kg phenol produced	Determination method	Emission control	Emission height, m
Feed purification vent				Liquid trap.	34.1
Peroxidation off gas scrubber vent			Sampled.	Scrubber and condenser.	38.1
	Cumene	2.7			
	Hydrocarbons[a]	3.2			
Cumene hydroperoxide concentration vent			Sampled.	Condenser.	12.2
	Cumene	0.33			
	Hydrocarbons	0.40			
Cleavage condenser vent				Condenser.	6.1
Acetone section scrubber vent				Scrubber.	36.6
Residual oil sump vent				None.	9.1
Phenolic water sump vent				None.	7.3
Pump drain sump vent				None.	21.3
Water scrubber stack				Scrubber.	26.4
Storage tank vents				Floating roofs, sealed roofs, and none.	
Fugitive emissions	Hydrocarbons	0.63			

Note.—Blanks indicate no information reported.

[a] Hydrocarbon emission factors are total nonmethane hydorcarbons determined by summing the methane equivalent (based on carbon content) emission factors for all nonmethane organic materials.

TABLE H-7. REPORTED EMISSIONS INFORMATION FOR PLANT 7

Emission point	Emission	Emission factor, g/kg phenol produced	Determination method	Emission control	Emission height, m
Spent air vent			Material balances.	Condensers	26.2
	Cumene	1.9			
	Hydrocarbons[a]	2.3			
Storage tank vents				Floating roofs, conservation vents, condensers, and none.	
Fugitive emissions	Minor				

Note.—Blanks indicate no information reported.

[a] Hydrocarbon emission factor is the cumene emission factor in methane equivalents, based on carbon content.

TABLE H-8. REPORTED EMISSIONS INFORMATION FOR PLANT 8[a]

Emission point	Emission	Emission factor, g/kg phenol produced	Determination method	Emission control	Emission height, m
Peroxidation vent			Engineering estimate.		
	Cumene	5.4			15.2
	Hydrocarbons[b]	6.5			
Cleavage vent			Engineering estimate		
	Cumene	0.071			4.6
	Acetone	0.042			15.2
	Hydrocarbons	0.12			20.4
Finishing vent			Engineering estimate.		
	Acetone	3.3			4.6
	Aldehydes	2.4			18.3
	Hydrocarbons	4.3			28.3
Recovery section			Engineering estimate.		
	Cumene	0.00089			0.6
	Hydrocarbons	0.0011			4.6
					28.3
Flare			Engineering estimate.		
	Carbon dioxide	1,500			1.2
Storage tank vents				Condensers and none.	
Fugitive emissions	No estimate.				

Note.—Blanks indicate no information reported.

[a] Not in operation.

[b] Hydrocarbon emission factors are the sum of the methane equivalent emission factors, based on carbon content for all nonmethane organic materials.

TABLE H-9. REPORTED EMISSION INFORMATION FOR THE GEORGIA-PACIFIC CORPORATION PLANT AT PLACQUEMINE, LOUISIANA, 1975

Emission point	Emission factor, g/kg phenol produced						Height, m
	Total nonmethane hydrocarbons[a]	Cumene	Acetone	Aromatics	Phenol	α-Methyl-styrene	
Peroxidation carbon adsorption vent	0.011	0.0088					26.2
Oxidizer vent condenser	0.073	0.061					23.2
Cumene recovery condenser vent	0.020	0.016					26.2
Oxidizer feed drum vent	0.0020	0.0017					
Recycle cumene tank vent	0.0085	0.0071					6.4
Cumene storage tank vent	0.17	0.14					9.8
Cleavage ejector condenser vent	0.011		0.013				23.2
Preflash ejector condneser vent	0.0012	0.0010					23.2
Cleavage tank condenser vent[b]							23.2
Spent caustic drum	0.0020			–[c]			4.5
Acetone tower jet condenser vent	0.0077		0.0093				24.7
Tower reflux drum vent	<0.00004						
α-Methylstyrene tower reflux drum vent	<0.00004						
α-Methylstyrene tower overhead vent[b]							
Tower purge separator vent	0.0033				0.0032		1.5
Phenolic water reflux vent	<0.00004						
Acetone tank scrubber vent	0.030		0.036				13.1
Acetone storage tank vent	2.5		3.0				9.8
Phenolic water tank vent	0.0020				0.0020		12.2
Phenol rundown tank vent	0.0065				0.0064		
Phenol storage tank vent	0.065						8.5
Heavy end tower feed tank vent	0.0053				0.0052		5.5
α-Methylstyrene tower feed tank vent	0.011						7.0
α-Methylstyrene tower rundown tank vent	0.0022					0.0002	8.2
α-Methylstyrene day tank vent	0.0006					0.0004	3.0
Acetone loading area	0.061	0	0.074				3.6
Phenol loading area	0.073				0.072		3.6
Phenol shipping area	0.13				0.12		6.1
Fugitive: pumps and sewers	0.022						

Note.—Blanks indicate material not reported.

[a] Total nonmethane hydrocarbon emission factors are the sum of the methane equivalent emission factors (based on carbon content) for all nonmethane organic materials.

[b] To be burned.

[c] Can not quantify.

APPENDIX I

DERIVATION OF SOURCE SEVERITY EQUATIONS

SUMMARY OF SEVERITY EQUATIONS

The severity of pollutants may be calculated using the mass emission rate, Q, the height of the emissions, H, and the threshold limit value, TLV. The equations summarized in Table I-1 are developed in detail in this appendix.

TABLE I-1. POLLUTANT SEVERITY EQUATIONS FOR ELEVATED POINT SOURCES

Pollutants	Severity equation
Particulate	$S = \frac{70\ Q}{H^2}$
SO_x	$S = \frac{50\ Q}{H^2}$
NO_x	$S = \frac{315\ Q}{H^{2.1}}$
Hydrocarbon	$S = \frac{162\ Q}{H^2}$
Carbon monoxide	$S = \frac{0.78\ Q}{H^2}$
Other	$S = \frac{5.5\ Q}{TLV \cdot H^2}$

DERIVATION OF χ_{max} FOR USE WITH U.S. AVERAGE CONDITIONS

The most widely accepted formula for predicting downwind ground level concentrations from a point source is (89):

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(I-1)}$$

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(89) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

where χ = downwind ground level concentration at reference coordinate x and y with emission height of H, g/m^3
Q = mass emission rate, g/s
π = 3.14
σ_y = standard deviation of horizontal dispersion, m
σ_z = standard deviation of vertical dispersion, m
$\bar{u}$ = wind speed, m/s
y = horizontal distance from centerline of dispersion, m
H = height of emission release, m
x = downwind dispersion distance from source of emission release, m

χ_{max} is assumed to occur when x is much greater than 0 and when y equals 0. For a given stability class, standard deviations of horizontal and vertical dispersion have often been expressed as a function of downwind distance by power law relationships as follows (90):

$$\sigma_y = ax^b \tag{I-2}$$

$$\sigma_z = cx^d + f' \tag{I-3}$$

Values for a, b, c, d, and f' are given in Tables I-2 (91) and I-3. Substituting these general equations into Equation I-1 yields:

$$\chi = \frac{Q}{ac\pi ux^{b+d} + a\pi uf'x^b} \exp\left[-\frac{H^2}{2(cx^d + f')^2}\right] \tag{I-4}$$

Assuming that χ_{max} occurs at x less than 100 m or the stability class is C, then f' equals 0 and Equation I-4 becomes:

$$\chi = \frac{Q}{ac\pi ux^{b+d}} \exp\left[\frac{-H^2}{2c^2x^{2d}}\right] \tag{I-5}$$

For convenience, let:

$$A_R = \frac{Q}{ac\pi u} \text{ and } B_R = \frac{-H^2}{2c^2}$$

so that Equation I-5 reduces to:

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(90) Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

(91) Tadmor, J., and Y. Gur. Analytical Expressions for the Vertical and Lateral Dispersion Coefficients in Atmospheric Diffusion. Atmospheric Environment, 3(6):688-689, 1969.

TABLE I-2. VALUES OF a FOR THE COMPUTATION OF σ_y[a] (91)

Stability class	a
A	0.3658
B	0.2751
C	0.2089
D	0.1471
E	0.1046
F	0.0722

[a] For the equation

$$\sigma_y = ax^b$$

where x = downwind distance
b = 0.9031 (from Reference 46)

TABLE I-3. VALUES OF THE CONSTANTS USED TO ESTIMATE VERTICAL DISPERSION[a] (90)

Usable range, m	Stability class	Coefficient		
		c_1	d_1	f_1'
>1,000	A	0.00024	2.094	-9.6
	B	0.055	1.098	2.0
	C	0.113	0.911	0.0
	D	1.26	0.516	-13
	E	6.73	0.305	-34
	F	18.05	0.18	-48.6
		c_2	d_2	f_2'
100 to 1,000	A	0.0015	1.941	9.27
	B	0.028	1.149	3.3
	C	0.113	0.911	0.0
	D	0.222	0.725	-1.7
	E	0.211	0.678	-1.3
	F	0.086	0.74	-0.35
		c_3	d_3	f_3'
<100	A	0.192	0.936	0
	B	0.156	0.922	0
	C	0.116	0.905	0
	D	0.079	0.881	0
	E	0.063	0.871	0
	F	0.053	0.814	0

[a] For the equation

$$\sigma_z = cx^d + f'$$

$$\chi = A_R x^{-(b+d)} \exp\left[\frac{B_R}{x^{2d}}\right] \qquad \text{(I-6)}$$

making the first derivative of Equation I-6

$$\frac{d\chi}{d} = A_R \left\{ x^{-b-d}\left(\exp\left[B_R x^{-2d}\right]\right)\left(-\ 2dB_R x^{-2d-1}\right) + \exp\left[B_R x^{-2d}\right]\left(-\ b - d\right)x^{-b-d-1} \right\} \qquad \text{(I-7)}$$

and setting this equal to zero (to determine the roots which give the minimum and maximum conditions of χ with respect to x) yields:

$$\frac{d\chi}{dx} = 0 = A_R x^{-b-d-1}\left(\exp\left[B_R x^{-2d}\right]\right)\left[-\ 2dB_R x^{-2d} - b - d\right] \qquad \text{(I-8)}$$

Since we define that $x \neq 0$ or ∞ at χ_{max}, the following expression must be equal to 0:

$$-\ 2dB_R x^{-2d} - d - b = 0 \qquad \text{(I-9)}$$

or

$$(b + d)x^{2d} = -\ 2dB_R \qquad \text{(I-10)}$$

or

$$x^{2d} = \frac{-\ 2dB_R}{b + d} = \frac{2d\ H^2}{2c^2(b + d)} \qquad \text{(I-11)}$$

or

$$x^{2d} = \frac{d\ H^2}{c^2(b + d)} \qquad \text{(I-12)}$$

or

$$x = \left(\frac{d\ H^2}{c^2(b + d)}\right)^{1/2d} \text{ at } \chi_{max} \qquad \text{(I-13)}$$

Thus Equations I-2 and I-3 become:

$$\sigma_y = a\left(\frac{d\ H^2}{c^2(d + b)}\right)^{b/2d} \qquad \text{(I-14)}$$

$$\sigma_z = c\left(\frac{d\ H^2}{c^2(b + d)}\right)^{d/2d} = \left(\frac{d\ H^2}{b + d}\right)^{1/2} \qquad \text{(I-15)}$$

The maximum will be determined for U.S. average conditions of stability. According to Gifford (92), this is when $\sigma_y = \sigma_z$.

Since b = 0.9031, and upon inspection of Table I-3 under U.S. average conditions, $\sigma_y = \sigma_z$, it can be seen that $0.881 \le d \le 0.905$ (class C stability[a]). Thus, it can be assumed that b is nearly equal to d or:

$$\sigma_z = \frac{H}{\sqrt{2}} \qquad \text{(I-16)}$$

and

$$\sigma_y = \frac{a}{c}\left(\frac{H}{\sqrt{2}}\right) \qquad \text{(I-17)}$$

Under U.S. average conditions, $\sigma_y = \sigma_z$ and $a \cong c$ if $b \cong d$ and $f' = 0$ (between class C and D, but closer to belonging in class C).

Then

$$\sigma_y = \frac{H}{\sqrt{2}} \qquad \text{(I-18)}$$

Substituting for σ_y and σ_z into Equation I-1 and letting $y = 0$:

$$\chi_{max} = \frac{2\ Q}{\pi u H^2} \exp\left[-\frac{1}{2}\left(\frac{H\sqrt{2}}{H}\right)^2\right] \qquad \text{(I-19)}$$

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[a] The values given in Table I-3 are mean values for stability class. Class C stability describes these coefficients and exponents, only within about a factor of two (89).

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(92) Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

or

$$\chi_{max} = \frac{2\ Q}{\pi e u H^2} \qquad \text{(I-20)}$$

For U.S. average conditions, u = 4.47 m/s so that Equation I-20 reduces to:

$$\chi_{max} = \frac{0.0524\ Q}{H^2} \qquad \text{(I-21)}$$

DEVELOPMENT OF SOURCE SEVERITY EQUATIONS

The general source severity, S, relationship has been defined as follows:

$$S = \frac{\overline{\chi}_{max}}{F} \qquad \text{(I-22)}$$

where $\overline{\chi}_{max}$ = maximum time-averaged ground level concentration

F = hazard factor defined as the ambient air quality standard for criteria pollutants and a modified TLV (i.e., TLV • 8/24 • 1/100) for noncriteria pollutants

Noncriteria Emissions

The value of $\overline{\chi}_{max}$ may be derived from χ_{max}, an undefined "short-term" (t_o) concentration. An approximation for longer term concentration (t_1) may be made as follows (89):

For a 24-hr time period,

$$\overline{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t_1}\right)^{0.17} \qquad \text{(I-23)}$$

or

$$\overline{\chi}_{max} = \chi_{max}\left(\frac{3\ \text{min}}{1,440\ \text{min}}\right)^{0.17} \qquad \text{(I-24)}$$

$$\overline{\chi}_{max} = \chi_{max}\ (0.35) \qquad \text{(I-25)}$$

Since the hazard factor is defined and derived from TLV values as follows:

$$F = (\mathrm{TLV}) \left(\frac{8}{24}\right)\left(\frac{1}{100}\right) \tag{I-26}$$

$$F = (3.33 \times 10^{-3})\ \mathrm{TLV} \tag{I-27}$$

then the severity factor, S, is defined as:

$$S = \frac{\overline{\chi}_{max}}{F} = \frac{(0.35)\chi_{max}}{(3.33 \times 10^{-3})\ \mathrm{TLV}} \tag{I-28}$$

$$S = \frac{105\ \chi_{max}}{\mathrm{TLV}} \tag{I-29}$$

If a weekly averaging period is used, then:

$$\overline{\chi}_{max} = \chi_{max} \left(\frac{3}{10{,}080}\right)^{0.17} \tag{I-30}$$

or

$$\overline{\chi}_{max} = (0.25)\chi_{max} \tag{I-31}$$

and

$$F = (\mathrm{TLV})\left(\frac{40}{168}\right)\left(\frac{1}{100}\right) \tag{I-32}$$

$$F \qquad 8 \times 10^{-3})\mathrm{TLV} \tag{I-33}$$

and the severity factor, S, is:

$$S = \frac{\overline{\chi}_{max}}{F} = \frac{(0.25)\chi_{max}}{(2.38 \times 10^{-3})\mathrm{TLV}} \tag{I-34}$$

or

$$S = \frac{105\chi_{max}}{\mathrm{TLV}} \tag{I-35}$$

which is entirely consistent, since the TLV is being corrected for a different exposure period.

Therefore, the severity can be derived from χ_{max} directly without regard to averaging time for noncriteria emissions. Thus, combining Equations I-35 and I-21, for elevated sources, gives:

$$S = \frac{5.5\ Q}{TLV \cdot H^2} \qquad (I\text{-}36)$$

Criteria Emissions

For the criteria pollutants, established standards may be used as F values in Equation I-22. These are given in Table I-4. However, Equation I-23 must be used to give the appropriate averaging period. These equations are developed for elevated sources using Equation I-21.

TABLE I-4. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS (93)

Pollutant	Averaging time	Primary standards	Secondary standards
Particulate matter	Annual (geometric mean)	75 $\mu g/m^3$	60[a] $\mu g/m^3$
	24-hour[b]	260 $\mu g/m^3$	160 $\mu g/m^3$
SO_x	Annual (arithmetic mean)	80 $\mu g/m^3$	60 $\mu g/m^3$
	24-hour[b]	365 $\mu g/m^3$	260[c] $\mu g/m^3$
	3-hour[b]	-	1,300 $\mu g/m^3$
Carbon monoxide	8-hour[b]	10,000 $\mu g/m^3$	
	1-hour[b]	40,000 $\mu g/m^3$	(Same as primary)
Nitrogen dioxide	Annual (arithmetic mean)	100 $\mu g/m^3$	(Same as primary)
Photochemical oxidants	1-hour[b]	160 $\mu g/m^3$	(Same as primary)
Hydrocarbons (nonmethane)	3-hour (6 a.m. to 9 a.m.)	160 $\mu g/m^3$[d]	(Same as primary)

[a] The secondary annual standard (60 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the 24-hour secondary standard.

[b] Not to be exceeded more than once per year.

[c] The secondary annual standard (260 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the annual standard.

[d] There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used for hydrocarbons in this report is an EPA recommended guideline for meeting the primary ambient air quality standard for oxidants.

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(93) Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

Carbon Monoxide Severity--
The primary standard for CO is reported for a 1-hr averaging time. Therefore,

$$t = 60 \text{ min}$$

$$t_o = 3 \text{ min}$$

$$\overline{\chi}_{max} = \chi_{max}\left(\frac{3}{60}\right)^{0.17} \qquad \text{(I-37)}$$

$$= \frac{2\ Q}{\pi e u H^2}\left(\frac{3}{60}\right)^{0.17} \qquad \text{(I-38)}$$

$$= \frac{2\ Q}{(3.14)(2.72)(4.5)H^2}\ (0.6) \qquad \text{(I-39)}$$

$$\overline{\chi}_{max} = \frac{0.052\ Q}{H^2}\ (0.6) \qquad \text{(I-40)}$$

$$\overline{\chi}_{max} = \frac{(3.12 \times 10^{-2})Q}{H^2} \qquad \text{(I-41)}$$

$$\text{Severity, } S = \frac{\overline{\chi}_{max}}{F} \qquad \text{(I-42)}$$

Setting F equal to the primary standard for CO, i.e., 0.04 g/m^3, yields:

$$S = \frac{\overline{\chi}_{max}}{F} = \frac{(3.12 \times 10^{-2})Q}{0.04\ H^2} \qquad \text{(I-43)}$$

or

$$S_{CO} = \frac{0.78\ Q}{H^2} \qquad \text{(I-44)}$$

Hydrocarbon Severity--
The primary standard for hydrocarbon is reported for a 3-hr averaging time.

$$t_1 = 180 \text{ min}$$

$$t_o = 3 \text{ min}$$

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{180}\right)^{0.17} \tag{I-45}$$

$$= 0.5\chi_{max} \tag{I-46}$$

$$= \frac{(0.5)(0.052)\ Q}{H^2} \tag{I-47}$$

$$\bar{\chi}_{max} = \frac{0.026\ Q}{H^2} \tag{I-48}$$

For hydrocarbons, the concentration of 1.6×10^{-4} g/m^3 has been issued as a guideline for achieving oxidant standards. Therefore,

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{0.026\ Q}{1.6 \times 10^{-4}\ H^2} \tag{I-49}$$

or

$$S_{HC} = \frac{162.5\ Q}{H^2} \tag{I-50}$$

Particulate Severity--

The primary standard for particulate is reported for a 24-hr averaging time.

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{1,440}\right)^{0.17} \tag{I-51}$$

$$= \frac{(0.052)\ Q\ (0.35)}{H^2} \tag{I-52}$$

$$\bar{\chi}_{max} = \frac{(0.0182)\ Q}{H^2} \tag{I-53}$$

For particulates, $F = 2.6 \times 10^{-4}$ g/m^3, and

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{0.0182\ Q}{2.6 \times 10^{-4}\ H^2} \tag{I-54}$$

$$S_P = \frac{70\ Q}{H^2} \qquad \text{(I-55)}$$

SO_x Severity--
The primary standard for SO_x is reported for a 24-hr averaging time. Using t_1 = 1,440 minutes and proceeding as before:

$$\bar{\chi}_{max} = \frac{(0.0182)\ Q}{H^2} \qquad \text{(I-56)}$$

The primary standard is 3.65 x 10^{-4} g/m^3,

and

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.0182)Q}{3.65 \times 10^{-4}\ H^2} \qquad \text{(I-57)}$$

or

$$S_{SO_x} = \frac{50\ Q}{H^2} \qquad \text{(I-58)}$$

NO_x Severity--
Since NO_x has a primary standard with a 1-yr averaging time, the χ_{max} correction equation cannot be used. As an alternative, the following equation was selected:

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)\right]^2 \qquad \text{(I-59)}$$

A difficulty arises, however, because a distance x, from emission point to receptor, is included; hence, the following rationale is used:

The equation $\chi_{max} = \frac{2\ Q}{\pi e u H^2}$

is valid for neutral conditions or when $\sigma_z \cong \sigma_y$. This maximum occurs when

$$H \cong \sqrt{2}\sigma_z \qquad \text{(I-60)}$$

and since, under these conditions,

$$\sigma_z = ax^b \qquad \text{(I-61)}$$

then the distance, x_{max}, where the maximum concentration occurs is:

$$x_{max} = \left(\frac{H}{\sqrt{2a}}\right)^{\frac{1}{b}} \tag{I-62}$$

For class C conditions,

$$a = 0.113$$

$$b = 0.911$$

Simplifying Equation I-59,

$$\sigma_z = 0.113\ x_{max}^{0.911} \tag{I-63}$$

and

$$u = 4.5\ m/s$$

Letting $x = x_{max}$ in Equation I-59,

$$\bar{\chi} = \frac{4\ Q}{x_{max}^{1.911}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \tag{I-64}$$

where

$$x_{max} = \left(\frac{H}{0.16}\right)^{1.098} \tag{I-65}$$

$$x_{max} = 7.5\ H^{1.098} \tag{I-66}$$

and

$$\frac{4\ Q}{x_{max}^{1.911}} = \frac{4\ Q}{(7.5\ H^{1.098})^{1.911}} \tag{I-67}$$

Therefore,

$$\bar{\chi} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \tag{I-68}$$

$$\sigma_z = 0.113x^{0.911} \tag{I-69}$$

$$\sigma_z = 0.113\ (7.5\ H^{1.1})^{0.911} \qquad \text{(I-70)}$$

$$\sigma_z = 0.71\ H \qquad \text{(I-71)}$$

Therefore,

$$\overline{\chi} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{0.71\ H}\right)^2\right] \qquad \text{(I-72)}$$

$$= \frac{0.085\ Q}{H^{2.1}}\ (0.371) \qquad \text{(I-73)}$$

$$\overline{\chi} = \frac{3.15 \times 10^{-2}\ Q}{H^{2.1}} \qquad \text{(I-74)}$$

Since the NO_x standard is 1.0×10^{-4} g/m³, the NO_x severity equation is:

$$S_{NO_x} = \frac{(3.15 \times 10^{-2})\ Q}{1 \times 10^{-4}\ H^{2.1}} \qquad \text{(I-75)}$$

$$S_{NO_x} = \frac{315\ Q}{H^{2.1}} \qquad \text{(I-76)}$$

AFFECTED POPULATION CALCULATION

Another form of the plume dispersion equation is needed to calculate the affected population since the population is assumed to be distributed uniformly around the source. If the wind directions are taken to 16 points and it is assumed that the wind directions within each sector are distributed randomly over a period of a month or a season, it can be assumed that the effluent is uniformly distributed in the horizontal within the sector. The appropriate equation for average concentration, $\overline{\chi}$, in g/m³ is then (for 100 m $\leq$ x $\leq$ 1,000 m and stability class C) (94):

$$\overline{\chi} = \frac{2.03\ Q}{\sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(I-59)}$$

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(94) Schwartz, W. A., et al. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Volume I: Carbon Black Manufacturing by the Furnace Process. EPA-450/3-73-006a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 116 pp.

To find the distances at which $\overline{\chi}/F = 0.1$, roots are determined for the following equation:

$$\frac{2.03\ Q}{F\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] = 0.1 \qquad \text{(I-77)}$$

keeping in mind that:

$$\sigma_z = ax^b + f'$$

where a, b, and f' are functions of atmospheric stability and are assumed to be selected for stability Class C. Since Equation I-77 is a transcendental equation, the roots are found by an iterative technique using the computer.

For a specified emission from a typical source, $\overline{\chi}/F$ as a function of distance might look as follows:

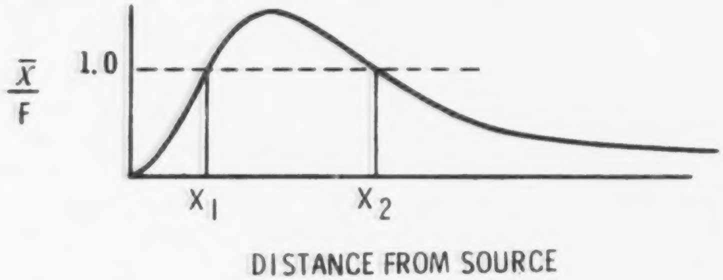


Figure I-1. $\frac{\overline{\chi}}{F}$ as a function of distance from source.

The affected population is contained in the area

$$A = \pi(x_2^2 - x_1^2) \qquad \text{(I-78)}$$

If the affected population density is D_p, the total affected population, P, is

$$P = D_pA \text{ (persons)} \qquad \text{(I-79)}$$

APPENDIX J

SIMULATED SOURCE SEVERITY DISTRIBUTIONS

Simulated source severity distributions for chemical substances emitted from the cumene peroxidation vent are presented in Figures J-1 through J-9.

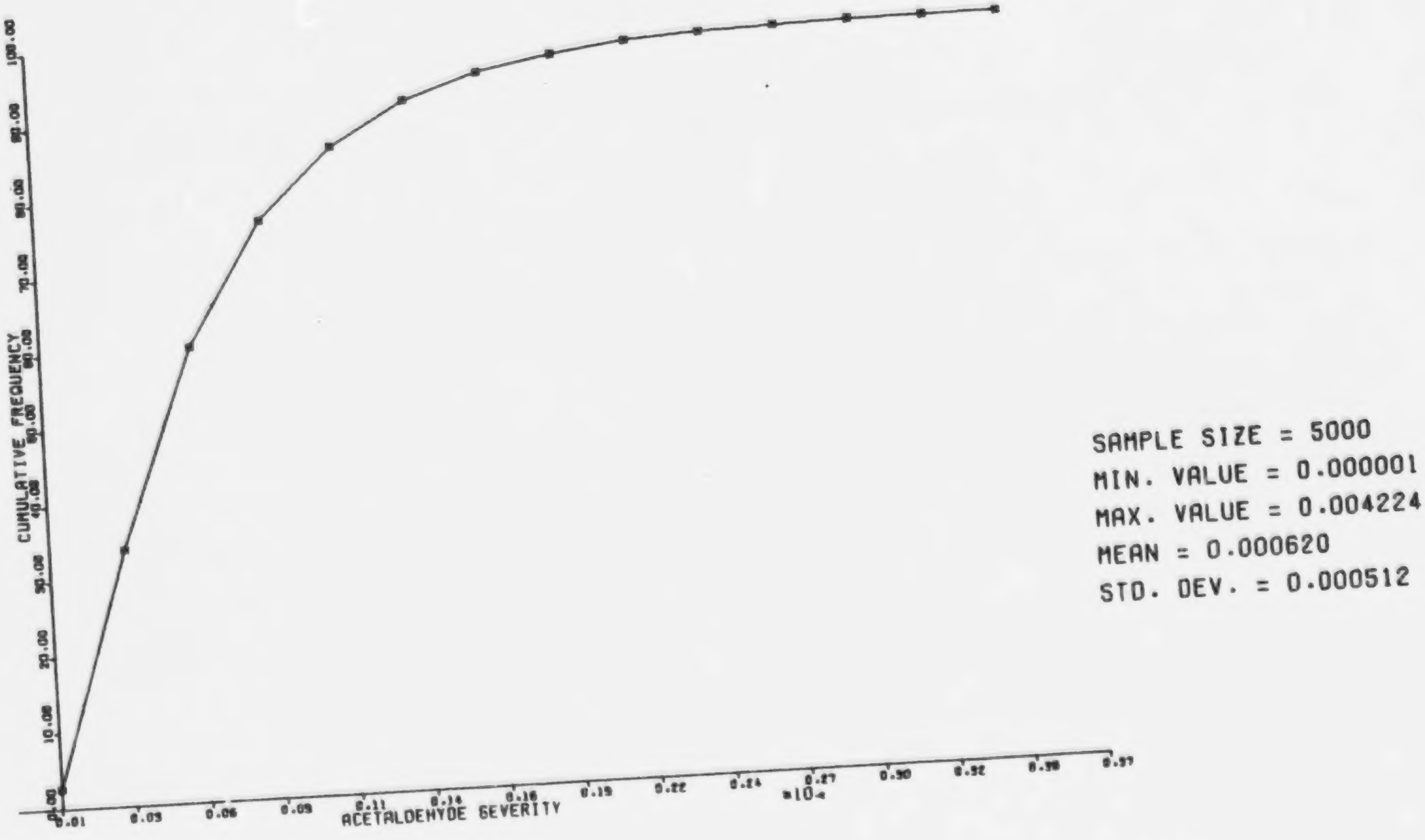


Figure J-1. Simulated source severity for acetaldehyde emitted from the cumene peroxidation vent.

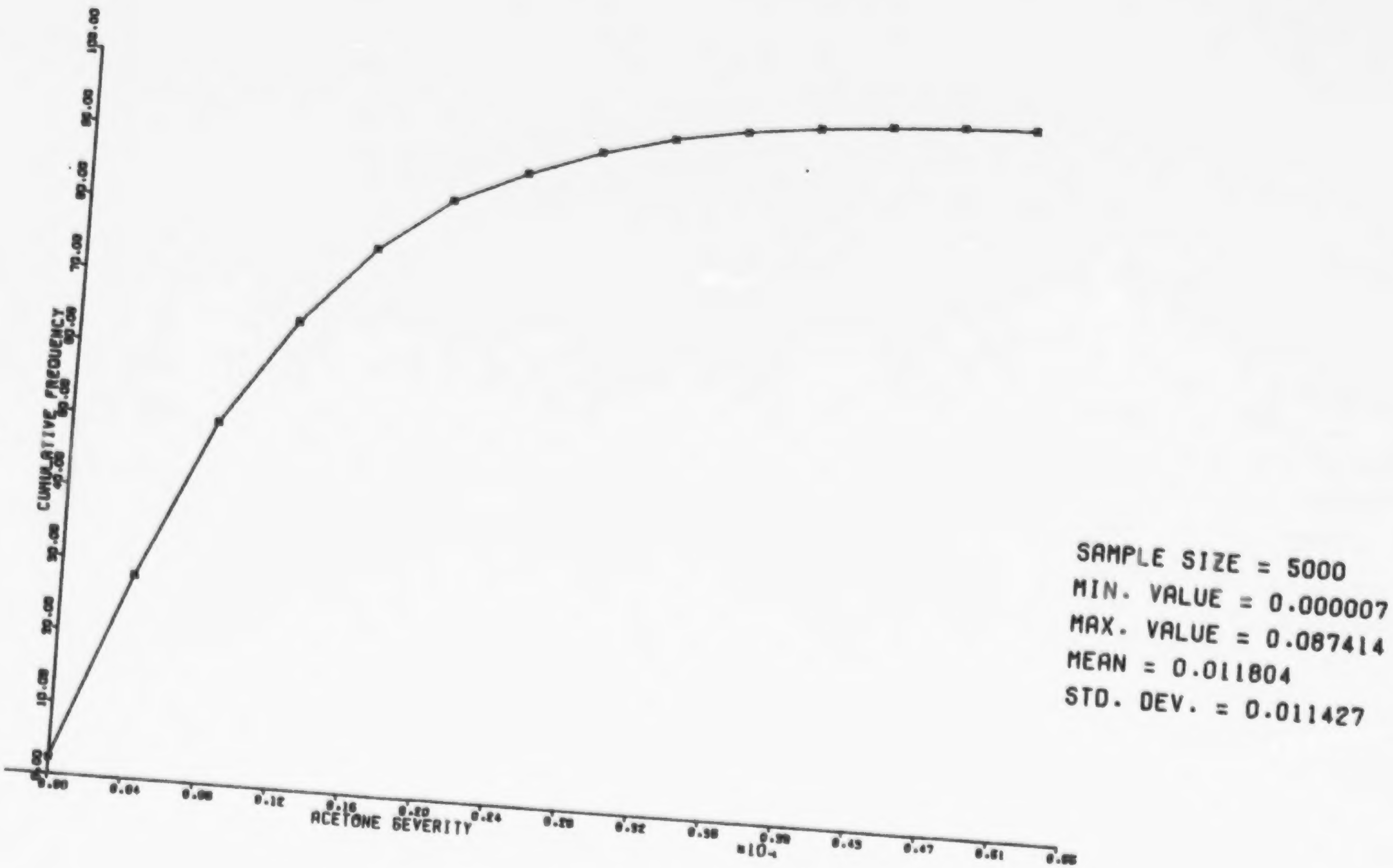
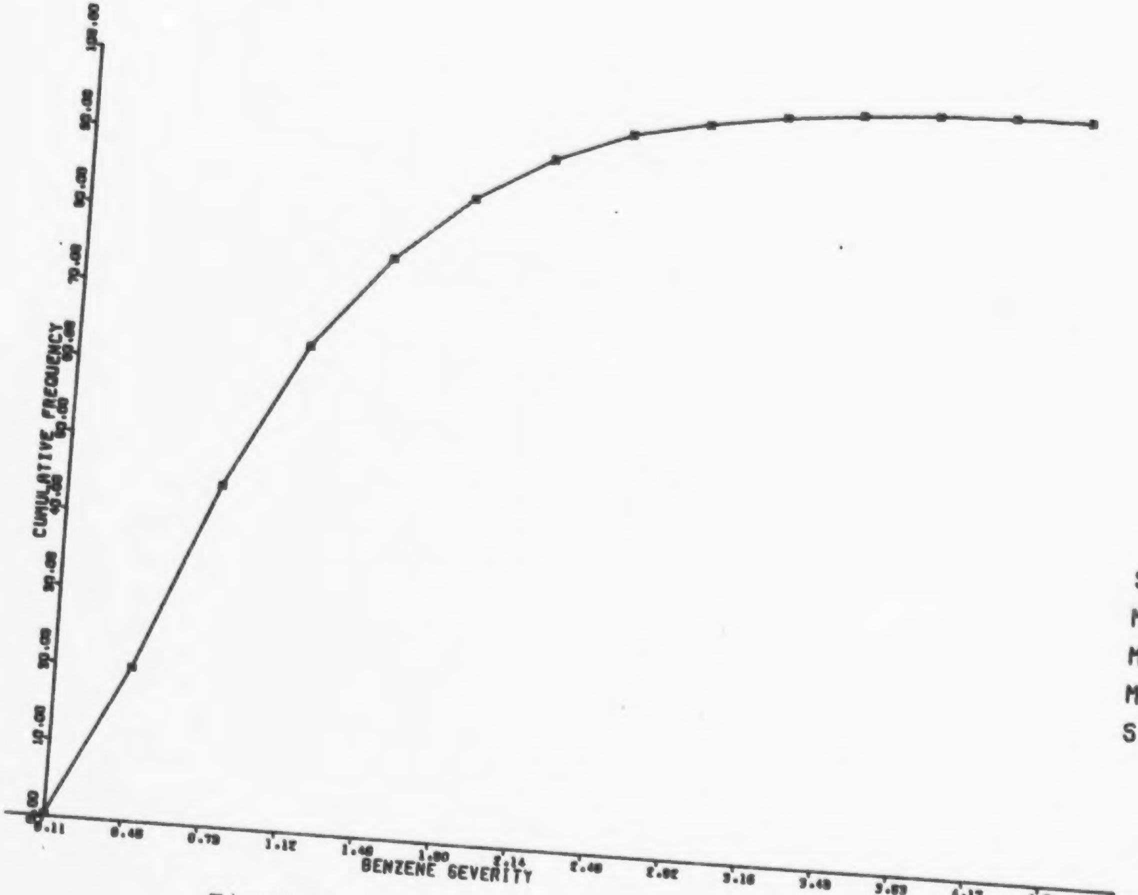


Figure J-2. Simulated source severity for acetone emitted from the cumene peroxidation vent.



SAMPLE SIZE = 5000
MIN. VALUE = 0.081986
MAX. VALUE = 4.908799
MEAN = 1.080967
STD. DEV. = 0.770110

Figure J-3. Simulated source severity for benzene emitted from the cumene peroxidation vent.[a]

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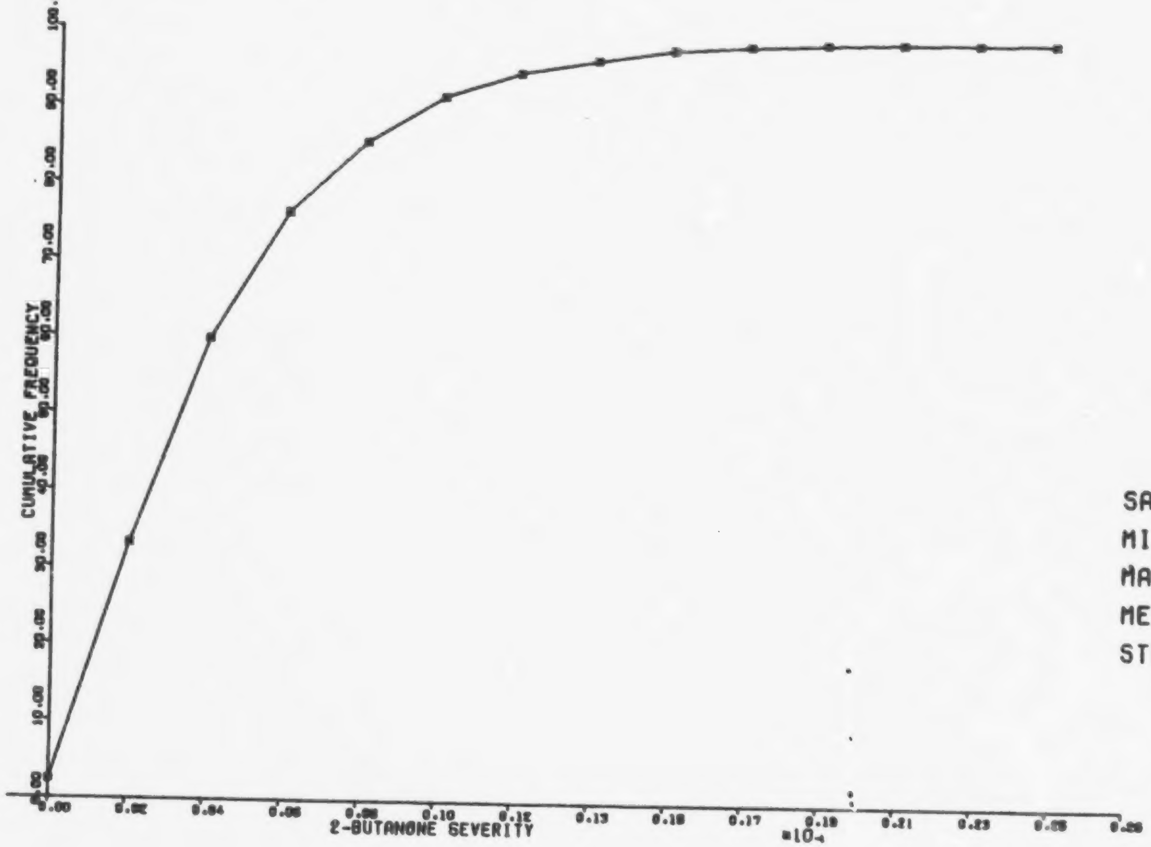
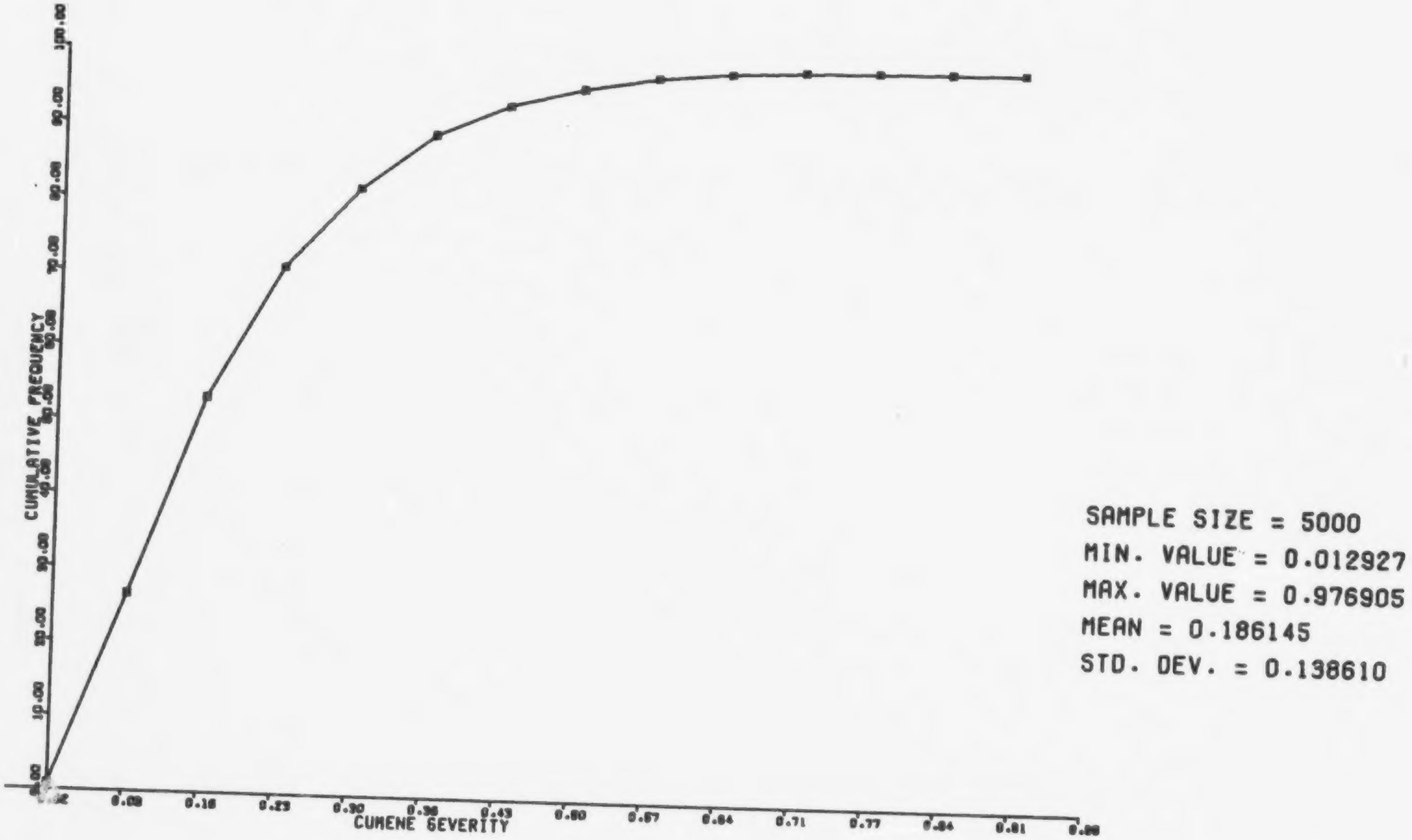
[a] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.



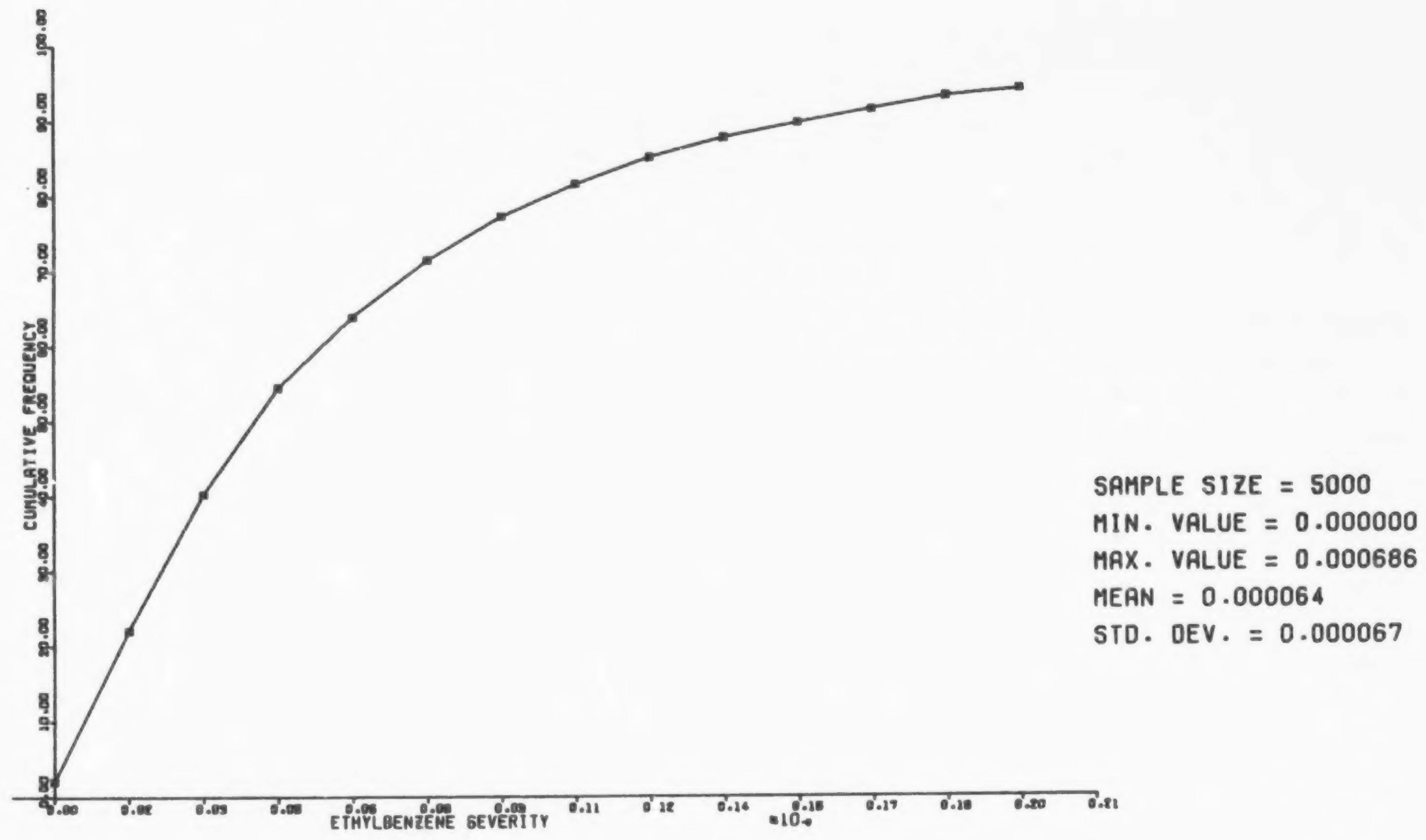
SAMPLE SIZE = 5000
MIN. VALUE = 0.000065
MAX. VALUE = 0.029486
MEAN = 0.004432
STD. DEV. = 0.003638

Figure J-4. Simulated source severity for 2-butanone emitted from the cumene peroxidation vent.



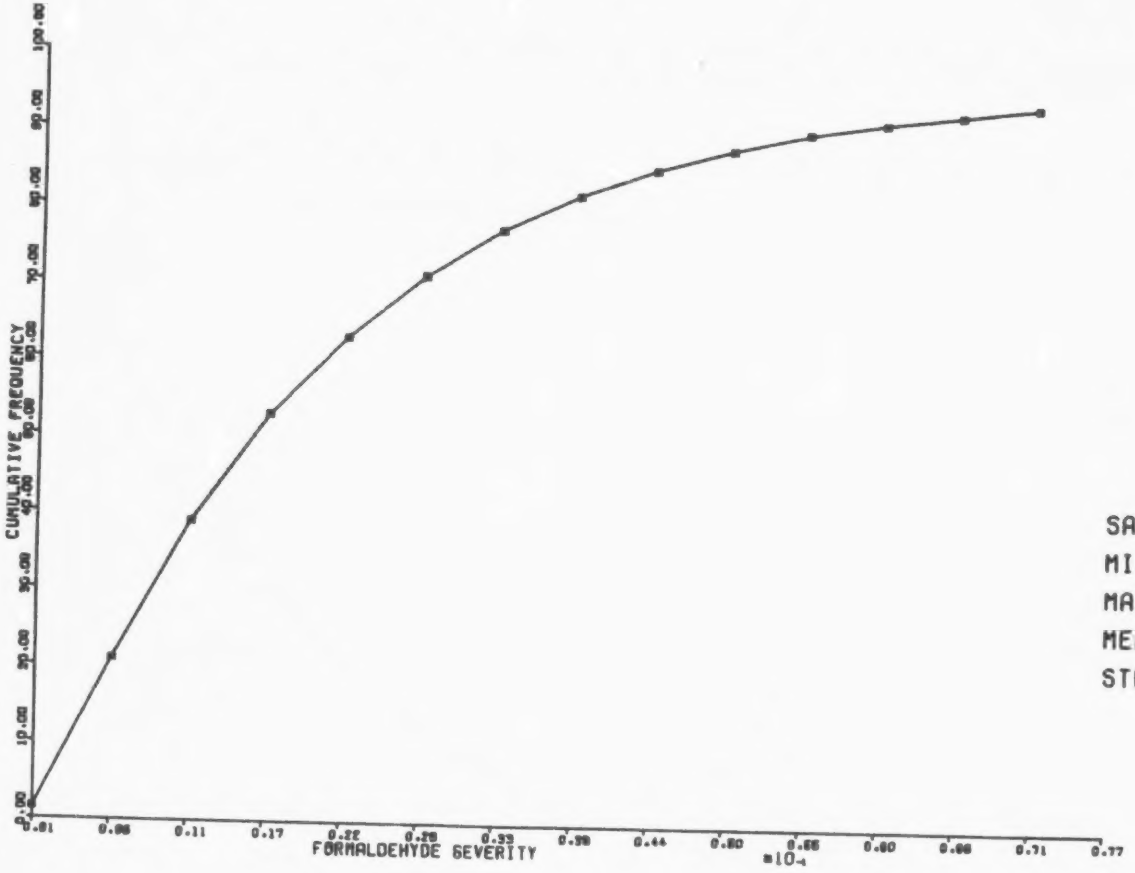
SAMPLE SIZE = 5000
MIN. VALUE = 0.012927
MAX. VALUE = 0.976905
MEAN = 0.186145
STD. DEV. = 0.138610

Figure J-5. Simulated source severity for cumene emitted from the cumene peroxidation vent.



SAMPLE SIZE = 5000
MIN. VALUE = 0.000000
MAX. VALUE = 0.000686
MEAN = 0.000064
STD. DEV. = 0.000067

Figure J-6. Simulated source severity for ethylbenzene emitted from the cumene peroxidation vent.



SAMPLE SIZE = 5000
MIN. VALUE = 0.000004
MAX. VALUE = 0.341705
MEAN = 0.023366
STD. DEV. = 0.024323

Figure J-7. Simulated source severity for formaldehyde emitted from the cumene peroxidation vent.

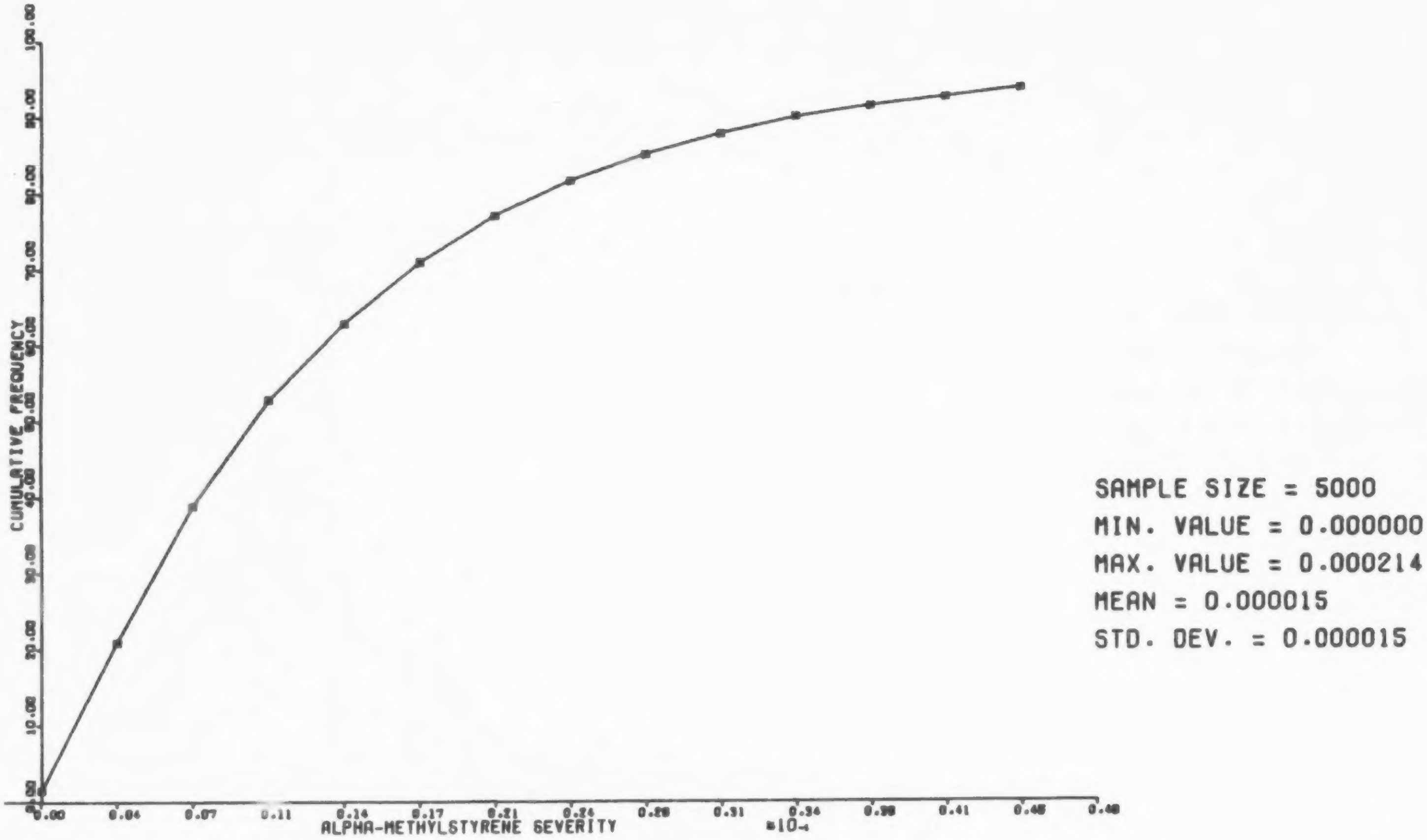
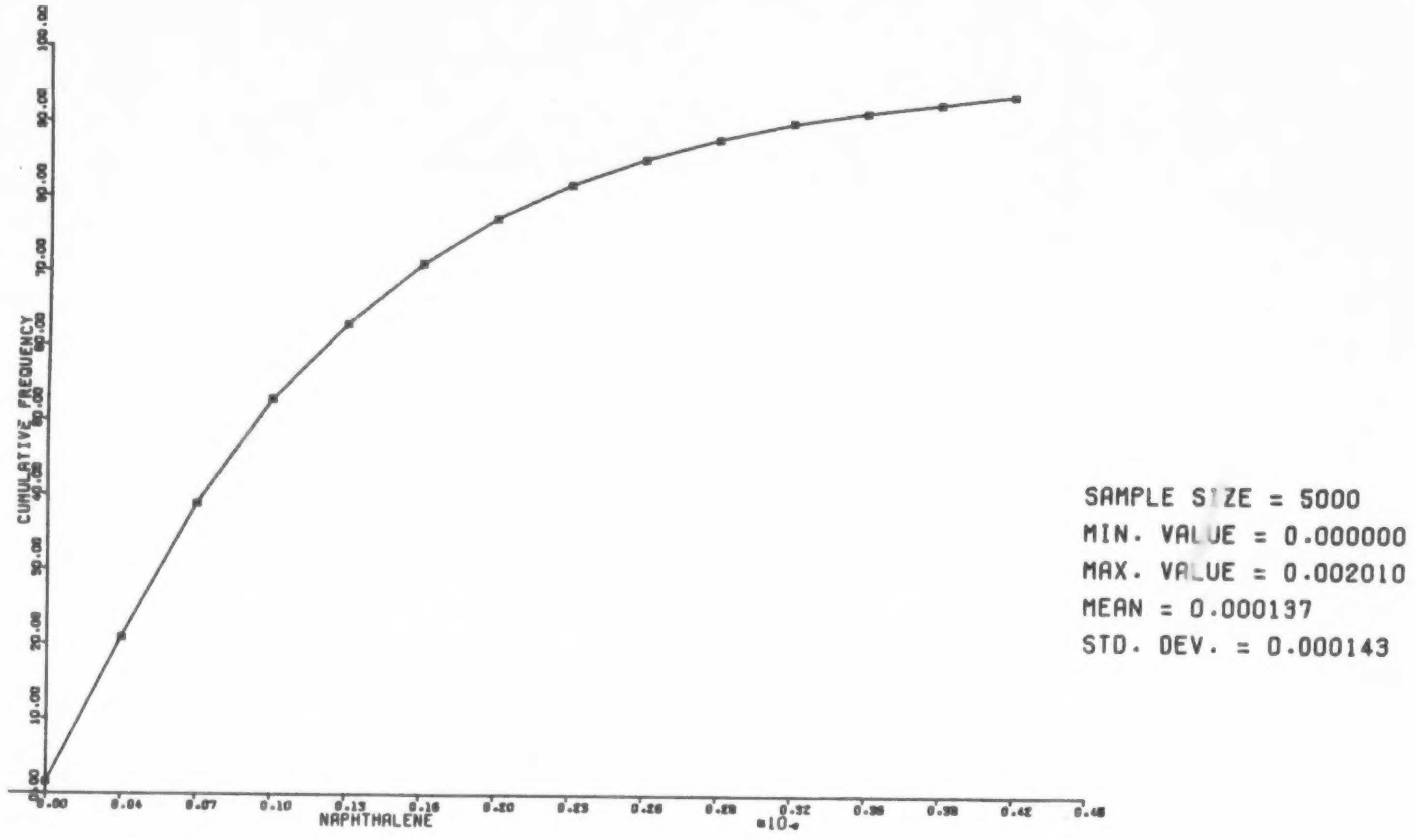


Figure J-8. Simulated source severity for α-methylstyrene emitted from the cumene peroxidation vent.



SAMPLE SIZE = 5000
MIN. VALUE = 0.000000
MAX. VALUE = 0.002010
MEAN = 0.000137
STD. DEV. = 0.000143

Figure J-9. Simulated source severity for naphthalene emitted from the cumene peroxidation vent.

APPENDIX K

AFFECTED POPULATION CALCULATIONS

Affected populations were calculated by the procedure outlined in Section 4 and Appendix I. Input data and results for the emission sources are shown in Tables K-1 to K-7 When the source severity is less than or equal to 0.1, the affected population is reported as zero.

TABLE K-1. ESTIMATED AFFECTED POPULATIONS: CUMENE PEROXIDATION VENT EMISSIONS FROM A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

	Data input						Data output			
Material[b]	Emission rate, g/s	Emission height, m	TLV, g/m³	Hazard factor,[a] g/m³	Wind speed, m/s	Population density, persons/km²	Root x_1,[c] km	Root x_2, km	Affected area,[d] km²	Affected population,[e] persons
Total nonmethane hydrocarbons	6.2	17.1	NA[f]	160×10^{-6}	4.5	1,333	0.96	1.7	6.2	8,300
Acetaldehyde	0.0072	17.1	0.180	6×10^{-4}	4.5	1,333	0	0	0	0
Acetone	2.1	17.1	2.400	0.0080	4.5	1,333	0	0	0	0
Benzene[g]	0.69	17.1	0.030	9.9×10^{-5}	4.5	1,333	0.076	0.68	0	0
2-Butanone	0.17	17.1	0.590	0.0020	4.5	1,333	0	0	0	0
Cumene	3.0	17.1	0.245	0.00082	4.5	1,333	0.087	0.46	0	0
Ethylbenzene	0.0014	17.1	0.435	0.0015	4.5	1,333	0	0	0	0
Formaldehyde	0.0034	17.1	0.003	1.0×10^{-5}	4.5	1,333	0	0	0	0
α-Methylstyrene	0.00034	17.1	0.480	0.0016	4.5	1,333	0	0	0	0
Naphthalene	0.00034	17.1	0.050	0.00017	4.5	1,333	0	0	0	0

[a] Hazard factor = TLV · 8/24 · 1/100 for noncriteria pollutants.

[b] Only materials which have TLV's or hazard factors are listed.

[c] The distance to the plant boundary is used when x_1 is less than 0.96 km.

[d] The affected area is reported as 0 when both x_1 and x_2 are less than 0.96 km, which is the distance to the plant boundary.

[e] The affected population is determined by multiplying the affected area by the capacity weighted mean county population density. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity, the population density may be lower or higher than the county average.

[f] Not applicable.

[g] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

TABLE K-2. ESTIMATED AFFECTED POPULATIONS: CLEAVAGE SECTION VENT EMISSIONS (COMBINED) FROM A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Material[b]	Data input						Data output			
	Emission rate, g/s	Emission height, m	TLV, g/m³	Hazard factor,[a] g/m³	Wind speed, m/s	Population density, persons/km²	Root x_1,[c] km	Root x_2, km	Affected area,[d] km²	Affected population, persons
Total nonmethane hydrocarbons	0.59	12.8	NA[e]	160×10^{-6}	4.5	1,333	0.056	0.49	0	0
Acetone	2.1×10^{-5}	12.8	2.400	0.0080	4.5	1,333	0	0	0	0
Benzene[f]	1.1×10^{-4}	12.8	0.030	9.9×10^{-5}	4.5	1,333	0	0	0	0
2-Butanone	6.2×10^{-6}	12.8	0.590	0.0020	4.5	1,333	0	0	0	0
Cumene	0.48	12.8	0.245	0.00082	4.5	1,333	0	0	0	0
Ethylbenzene	1.7×10^{-6}	12.8	0.435	0.0015	4.5	1,333	0	0	0	0
Formaldehyde	9.0×10^{-7}	12.8	0.003	1.0×10^{-5}	4.5	1,333	0	0	0	0

[a] Hazard factor = TLV • 8/24 • 1/100 for noncriteria pollutants.

[b] Only materials which have TLV's or hazard factors are listed.

[c] The distance to the plant boundary is used when x_1 is less than 0.96 km.

[d] The affected area is reported as 0 when both x_1 and x_2 are less than 0.96 km, which is the distance to the plant boundary.

[e] The affected population is determined by multiplying the affected area by the capacity weighted mean county population density. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity, the population density may be lower or higher than the county average.

[f] Not applicable.

[g] The benzene emission factors are not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

TABLE K-3. ESTIMATED AFFECTED POPULATIONS: PRODUCT PURIFICATION VENT EMISSIONS (COMBINED) FROM A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Material[b]	Data input						Data output			
	Emission rate, g/s	Emission height, m	TLV g/m³	Hazard factor[a] g/m³	Wind speed, m/s	Population density, persons/km²	Root x_1,[c] km	Root x_2, km	Affected area,[d] km²	Affected population,[e] persons
Total nonmethane hydrocarbons	4.1	26.5	NA[f]	160×10^{-6}	4.5	1,333	0.96	1.4	2.9	4,300

[a] Hazard factor = TLV • 8/24 • 1/100 for noncriteria pollutants.

[b] Only materials which have TLV's or hazard factors are listed.

[c] The distance to the plant boundary is used when x_1 is less than 0.96 km.

[d] The affected area is reported as 0 when both x_1 and x_2 are less than 0.96 km, which is the distance to the plant boundary.

[e] The affected population is determined by multiplying the affected area by the capacity weighted mean county population density. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity the population density may be lower or higher than the county average.

[f] Not applicable.

TABLE K-4. ESTIMATED AFFECTED POPULATIONS: STORAGE TANK VENT EMISSIONS FROM A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

	Data input						Data output			
Material[b]	Emission rate, g/s	Emission height, m	TLV, g/m^3	Hazard factor,[a] g/m^3	Wind speed, m/s	Population density, persons/km^2	Root x_1,[c] km	Root x_2, km	Affected area,[d] km^2	Affected population,[e] persons
Total nonmethane hydrocarbons	0.17	15.2	NA[f]	160×10^{-6}	4.5	1,333	0.12	0.19	0	0
Acetone	0.21	15.2	2.400	0.0080	4.5	1,333	0	0	0	0
Total nonmethane hydrocarbons	0.12	15.2	NA	160×10^{-6}	4.5	1,333	0	0	0	0
Cumene	0.097	15.2	0.245	0.00082	4.5	1,333	0	0	0	0
Total nonmethane hydrocarbons	0.0083	6.1	NA	160×10^{-6}	4.5	1,333	0	0	0	0
α-Methylstyrene	0.0069	6.1	0.480	0.0016	4.5	1,333	0	0	0	0
Total nonmethane hydrocarbons	0.047	9.1	NA	160×10^{-6}	4.5	1,333	0	0	0	0
Phenol[g]	0.047	9.1	0.019	6.3×10^{-5}	4.5	1,333	0.047	0.20	0	0
Total nonmethane hydrocarbons	0.1	15.2	NA	160×10^{-6}	4.5	1,333	0	0	0	0
Phenol[h]	0.1	15.2	0.019	6.3×10^{-5}	4.5	1,333	0.081	0.35	0	0

[a] Hazard factor = TLV · 8/24 · 1/100 for noncriteria pollutants.

[b] Only materials which have TLV's or hazard factors are listed.

[c] The distance to the plant boundary is used when x_1 is less than 0.96 km.

[d] The affected area is reported as 0 when both x_1 and x_2 are less than 0.96 km, which is the distance to the plant boundary.

[e] The affected population is determined by multiplying the affected area by the capacity weighted mean county population density. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity the population density may be lower or higher than the county average.

[f] Not applicable.

[g] Emission from heavy ends storage tank assumed to be phenol.

[h] The emission factor used is the average of a calculated value and an estimate supplied by H. Walker, Monsanto Chemical Intermediates Co., Alvin, Texas, 6 September 1978.

TABLE K-5. ESTIMATED AFFECTED POPULATIONS: PRODUCT TRANSPORT LOADING VENTS (COMBINED) AT A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Material[b]	Data input						Data output			
	Emission rate, g/s	Emission height, m	TLV g/m³	Hazard factor[a] g/m³	Wind speed, m/s	Population density, persons/km²	Root x_1,[c] km	Root x_2, km	Affected area,[d] km²	Affected population,[e] persons
Total nonmethane hydrocarbons	0.59	9.1	NA[f]	160×10^{-6}	4.5	1,333	0.034	0.50	0	0
Acetone	0.26	9.1	2.400	0.0080	4.5	1,333	0	0	0	0
Phenol	0.38[g]	9.1	0.019	6.3×10^{-5}	4.5	1,333	0.032	0.65	0	0

[a] Hazard factor = TLV · 8/24 · 1/100 for noncriteria pollutants.

[b] Only materials which have TLV's or hazard factors are listed.

[c] The distance to the plant boundary is used when x_1 is less than 0.96 km.

[d] The affected area is reported as 0 when both x_1 and x_2 are less than 0.96 km, which is the distance to the plant boundary.

[e] The affected population is determined by multiplying the affected area by the capacity weighted mean county population density. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity the population density may be lower or higher than the county average.

[f] Not applicable.

[g] The emission factor is an average of two estimates.

TABLE K-6. ESTIMATED AFFECTED POPULATIONS: FUGITIVE EMISSIONS[a] FROM A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Material[b]	Data input						Data output			
	Emission rate, g/s	Emission height, m	TLV, g/m³	Hazard factor,[c] g/m³	Wind speed, m/s	Population density, persons/km²	Root[d] x_1, km	Root x_2, km	Affected area,[e] km²	Affected population,[f] persons
Total nonmethane hydrocarbons	0.076	4.6	NA[g]	160×10^{-6}	4.5	1,333	0.018	0.17	0	0

[a] The fugitive emissions estimate includes those from pumps and sewers only. The other sources of fugitive emissions are not included in this estimate.

[b] Only materials which have TLV's or hazard factors are listed.

[c] Hazard factor = TLV • 8/24 • 1/100 for noncriteria pollutants.

[d] The distance to the plant boundary is used when x_1 is less than 0.96 km.

[e] The affected area is reported as 0 when both x_1 and x_2 are less than 0.96 km, which is the distance to the plant boundary.

[f] The affected population is determined by multiplying the affected area by the capacity weighted mean county population density. The population is, of course, not distributed uniformly throughout the county; therefore, in the plant vicinity the population density may be lower or higher than the county average.

[g] Not applicable.

APPENDIX L

PLUME RISE CORRECTION

Factors designed to quantify the potential hazard of manufacture of acetone and phenol from cumene were generated in Section 4 using the Gaussian plume equation to predict ground level concentrations. These factors are source severity and affected population. The Gaussian plume equation contains a factor called the effective stack heigh, H. This is equal to the sum of the physical stack height, h', and the amount of plume rise, ΔH; $H = h' + \Delta H$ (L-1). An exhaust plume rises before dispersal due to its exit velocity and temperature. This plume rise for plants manufacturing acetone and phenol from cumene is not a significant effect, that is:

$$\Delta H/h' \le 50\% \qquad \text{(L-2)}$$

In Section 4, source severity and affected population were therefore calculated assuming no plume rise; i.e., the effective emission height was equated with the physical stack height.

DETERMINATION OF PLUME RISE

Plume rise can be estimated from the Holland formula (89):

$$\Delta H = \frac{V_s\, D_i}{U}\left[1.5 + (2.68 \times 10^{-3})\, p \left(\frac{T_s - T_a}{T_s}\right) D_i\right] \qquad \text{(L-3)}$$

where ΔH = plume rise; m
V_s = stack gas exit velocity, m/s
D_i = inside stack diameter, m
U = wind speed, m/s
p = atmospheric pressure, mb
T_s = stack gas temperature, °K
T_a = ambient temperature, °K.

Under Class C stability conditions ΔH is corrected by a factor of 1.10.

Using values from the material balance given in Table 7, the stack gas exit velocity can be found from

$$V_s = \left(\frac{E_s}{M_s}\right) Cap \bullet U \bullet k_1 \bullet k_5 \bullet \left(\frac{4}{\pi\ D_i{}^{-2}}\right) \qquad \text{(L-4)}$$

where E_s = g of stack gas per kg phenol produced
M_s = molecular weight of stack gas, g/g mole
Cap = representative source phenol capacity, kg/yr
U = utilization factor
k_1 = conversion constant, yr/s
k_5 = conversion constant, m^3/g mole.

The conversion constant, k_5, is determined using

$$k_5 = \frac{R\ T_s}{P_s} \qquad \text{(L-5)}$$

where T_s = stack gas temperature, °K
R = universal gas constant, $8.31 \times 10^{-3}\ \frac{kPa \bullet m^3}{g\ mole\ °K}$
P_s = stack gas pressure, kPa.

All gas streams are assumed to be ambient temperature (292°K) and atmospheric pressure (101.33 kPa) based on observations at the sampling sites. Therefore, $k_5 = 0.024\ m^3$/g mole.

Table L-1 presents the values of V_s, D_i, E_s, and M_s used to determine the estimated plume rise also shown in that table. The following values were used for all cases:

$\bar{u}$ = 4.5 m/s
p = 1,013 mb
$T_s = T_a$ = 292°K
Cap = 136×10^6 kg/yr
U = 0.80
$k_1 = 3.169 \times 10^{-8}$ yr/s
$k_5 = 0.024\ m^3$/g mole.

If plume rise is taken into account the source severity should be correct (multiplied) by the following factor:

$$\left(\frac{h'}{h' + \Delta H}\right)^2.$$

This is also presented in Table L-1. Table L-2 presents an example of the usage of this factor on source severities for the cumene peroxidation vent.

TABLE L-1. PLUME RISE ESTIMATES FOR A REPRESENTATIVE SOURCE MANUFACTURING ACETONE AND PHENOL FROM CUMENE

Equation variables	Cumene peroxidation vent	Combined cleavage section vent[a]	Combined product purification section vent[a]	Combined storage tank vent[a]	Combined product transport loading vent[a]
V_s, m/s	32.1	0.00532	0.342	0.00765	0.0105
D_i[b], m	0.508	0.152	0.152	0.152	0.152
E_s	2.236	0.140	1.20	0.141	0.184
M_s	28.4	120	16	84	80
ΔH, m	6.0	0.0003	0.02	0.0004	0.0006
h', m	17.1	12.8	26.5	13.3[c]	9.1
$\Delta H/h'$	35%	0.4%	0.08%	0.003%	0.007%
$\left(\frac{h'}{h' + \Delta H}\right)^2$[d]	0.55	1.0	1.0	1.0	1.0

[a] All vents in that section are treated as one vent.

[b] Estimated.

[c] Average of all storage tank heights.

[d] Plume rise correction factor for source severity where plume rise was treated as zero corrections.

TABLE L-2. SOURCE SEVERITIES OF ATMOSPHERIC EMISSIONS FROM THE CUMENE PEROXIDATION VENT WITH AND WITHOUT PLUME RISE AT A REPRESENTATIVE SOURCES MANUFACTURING ACETONE AND PHENOL FROM CUMENE, 1977

Material emitted	Source severity[a]	
	No plume rise[b]	With plume rise[c]
Criteria pollutants		
Total nonmethane hydrocarbons[d]	3.5	1.9
Chemical substances:[e]		
Acetaldehyde	<0.00076	<0.00042
Acetone	0.0090	0.0050
Benzene[f]	0.43	0.24
2-Butanone	0.055	0.030
Cumene	0.23	0.13
Ethylbenzene	0.000063	0.000035
Formaldehyde	0.022	0.012
α-Methylstyrene[g]	0.000014	0.0000077
Naphthalene	<0.00013	<0.000072

[a] Sampling performed.

[b] Calculated with no plume rise, that is, $H = h'$, where $h' = 17.1$ m.

[c] Calculated with plume rise, that is $H = h' + \Delta H$, where $h' = 17.1$ m and $\Delta H = 6.0$, by multipling by the correction factor, $(h'/h' + \Delta H)^2 = 0.55$.

[d] Source severity for total nonmethane organic materials will not equal the source severity for total nonmethane hydrocarbons. Source severities for the nonmethane organic materials are based on the toxicity of the chemicals. The source severity for total nonmethane hydrocarbons is based on the guideline for meeting the primary ambient air quality standard for photochemical oxidants.

[e] Only substances which have a TLV are listed.

(continued)

TABLE L-2 (continued)

[f] The benzene emission factor is not representative. A process upset at one of the two plants sampled resulted in a high level of benzene emissions.

[g] Assumed to be the α form. The GC/MS analysis does not distinguish among the forms.

GLOSSARY

absorber: Carbon adsorption column used to remove hydrocarbons from gaseous emissions.

affected population: Number of nonplant persons exposed to airborne materials which are present in concentrations greater than a determined hazard potential factor.

afterburner: See incinerator.

Allied process: Process for the manufacture of phenol and acetone from cumene licensed by Allied Chemical Corporation to others.

atmospheric stability class: Class used to designate degree of turbulent mixing in the atmosphere.

cleavage: Chemical reaction in which cumene hydroperoxide in the presence of a catalyst forms acetone and phenol.

criteria pollutant: Emission species for which ambient air quality standards have been established; these include particulates, sulfur oxides, nitrogen oxides, carbon monoxide, and nonmethane hydrocarbons.[a]

emission factor: Weight of material emitted to the atmosphere per unit of phenol produced; e.g., g material/kg product.

flare: Combustion device used for the ultimate disposal of small continuous flow hydrocarbon streams and intermittent hydrocarbon streams.

Hercules process: Process for the manufacture of phenol and acetone from cumene licensed by Hercules Corporation to others.

incinerator: Thermal oxidizer used for ultimate disposal of hydrocarbons.

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[a] There is no primary ambient air quality standard for hydrocarbons. The value, $160\ \mu g/m^3$, used in this report is a guideline for meeting the primary ambient air quality standard for photochemical oxidants.

methane equivalents: The amount of methane, based on carbon content, that an amount of organic material is equal to.

noncriteria pollutant: Emission species for which no ambient air quality standards have been established.

product transport loading facility: Facility used at phenol plants to load product phenol, acetone, and byproduct into railroad tank cars and tank trucks.

source severity: Ratio of the maximum mean ground level concentration of emitted species to the hazard factor for the species.

tank outage: Distance from liquid surface to the top of a fixed roof storage tank.

total nonmethane hydrocarbons: Total amount of all nonmethane organic materials, in methane equivalents.

vent condensers: Heat exchanger system used to remove hydrocarbons from gaseous streams by condensation.

CONVERSION FACTORS AND METRIC PREFIXES (95)

CONVERSION FACTORS

To convert from	To	Multiply by
Degree Celsius (°C)	Degree Fahrenheit (°F)	$t_F^\circ = 1.8\ t_C^\circ + 32$
Gram/kilogram (g/kg)	Pound/ton	2.000
Joule (J)	British thermal units (Btu)	9.475×10^{-4}
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilogram/second (kg/s)	Pound mass/hour (lb/hr)	7.937×10^{3}
Kilojoule/kilogram	British thermal unit/ pound (Btu/lb)	4.299×10^{-1}
Kilometer^2 (km^2)	Mile^2 (mi^2)	3.861×10^{-1}
Meter (m)	Foot	3.281
Meter (m)	Mile	6.215×10^{-4}
Meter^3 (m^3)	Barrel (42 gal)	6.293
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Meter^3 (m^3)	Gallon (U.S. liquid)	2.642×10^{2}
Meter^3 (m^3)	Liter	1.000×10^{3}
Meter^3/second (m^3/s)	Gal/min	1.585×10^{-4}
Metric ton	Ton (short, 2,000 lb mass)	1.102
Pascal (Pa)	Pounds-force/inch^2 (psi)	1.450×10^{-4}
Pascal (Pa)	Torr (mm Hg, 0°C)	7.501×10^{-3}
Second (s)	Minute	1.667×10^{-2}
Watt (w)	Horsepower	1.340×10^{-3}

PREFIXES

Prefix	Symbol	Multiplication factor	Example
mega	M	10^6	1 MPa = 1×10^6 pascals
kilo	k	10^3	1 kJ = 1×10^3 joules
milli	m	10^{-3}	1 mm = 1×10^{-3} meters
micro	μ	10^{-6}	1 μg = 1×10^{-6} gram
nano	n	10^{-7}	1 ng = 1×10^{-7} gram

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(95) Standard for Metric Practice. ANSI/ASTM Designation E 380-76$^\varepsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

PB 80 150592

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Tafel 2 from Über die Reinigung von Phenol aus dem Cumolverfahren

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appeared in Chem. Techn., 23. Jg., Heft 7, Juli 1971

EPA-600/2-79-019d
Pg 14 (Fig. 3)

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